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A STUDY OF OIL DISPERSION: THE ROLE OF MIXING AND WEATHERING

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A STUDY OF OIL DISPERSION: THE ROLE OF MIXING AND WEATHERING

by

Alfred Chau
Donald Mackay
Department of Chemical Engineering
University of Toronto
Toronto, Ontario

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SUMMARY

A review is presented of factors influencing the dispersion of crude oils on seawater using chemical dispersants.

In this study, various experimental approaches were attempted with a view to elucidating the underlying determinants of dispersant effectiveness. These include: dispersant delivery, oil-dispersant mixing, and oil weathering.

The mixing phenomena have been shown to be very complex and are probably impossible to model accurately. The best that can be hoped for is a set of empirical rules or observations which are supported by theoretical principles. Attempts have been made to identify the presence of an oil film which retards mixing, using interfacial viscosity and ice-contact experiments, but the results are not satisfactory. Dispersion data have been re-interpreted using a "triangular diagram" approach. This has produced some interesting insights, including the suggestion that dispersion may be limited by the volume of accessible water and a maximum achievable emulsion concentration. A model has been assembled to quantify the role of weathering on dispersant effectiveness and to elucidate the presence of a "time window" for dispersion.

RÉSUMÉ

On présente un compte rendu des facteurs influençant la dispersion de pétrole brut sur la mer à l'aide de dispersants chimiques.

Dans cette étude, diverses approches expérimentales sont utilisées en vue d'élucider les facteurs déterminant l'efficacité des dispersants et entres autres, l'application du dispersant, le mélange hydrocarbure-dispersant et l'altération des hydrocarbures.

On a démontré que les phénomènes du mélange sone très complexes et sont probablement difficiles à modéliser de façon précise. Au mieux, on peut s'attendre à obtenir un ensemble de règles ou d'observations empiriques basées sur des principes théoriques. On a tenté d'identifier la présence d'une pellicule d'hydrocarbures qui retarde le mélange, à l'aide d'expériences basées sur la viscosité interfaciale et le contact avec la glace, mais les résultats n'étaient pas satisfaisants. Les données des dispersions ont été réinterprétées à l'aide d'une méthode basée sur des "diagrammes triangulaires", qui a rendu possibles certaines observations intéressantes, dont provient l'hypothèse selon laquelle la dispersion peut être limitée par le volume d'eau disponible et par une concentration d'émulsion maximum obtenable. Un modèle a été élaboré pour quantifier le rôle de l'altération sur l'efficacité du dispersant et pour élucider la présence d'un "créneau temporel" pour la dispersion.

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1. INTRODUCTION

As has been discussed widely in the literature, laboratory dispersion test systems demonstrate convincingly that relatively small quantities of chemical dispersants can have dramatic effects on the dispersability of crude oils. Results from large scale experimental spills have, however, often been less satisfactory. It appears that when dispersant is added in appropriate quantities to a slick at sea, there is often less dispersion than expected (Nicholls and Parker, 1985). Part of the difficulty has been the problem of measuring accurately the amount of oil which has actually been dispersed, or the amount which has remained on the surface. But it is increasingly apparent that there are fundamental factors which adversely affect oceanic dispersant performance. In this report we discuss and investigate three possible factors: dispersant delivery, oil weathering, and oil-dispersant mixing. The delivery aspect has been discussed previously (Mackay et al., 1986) and will only be reviewed briefly here. The weathering issue has been largely ignored, and it is thus appropriate to devote more attention to it here. The mixing issue is very difficult to investigate, and is the subject of some exploratory study as part of this work. The primary purpose is to address the weathering issue in a systematic manner in the hope that future studies may elucidate its true importance. Fortunately, the weathering issue is amenable to reproducible laboratory investigation.

The Mechanism of Dispersion

It is becoming increasingly clear that there are three stages which must be successfully completed for dispersion to occur.

First, a reasonable volume of dispersant must be delivered to the oil. It is generally accepted that a reasonable volume is 1 part dispersant to 20 parts oil, recognizing that much of this dispersant may not eventually usefully disperse the oil. Some factors which influence this delivery process are as follows:

(a) Oil of thickness 1 mm is equivalent to 10000 L/ha, thus to achieve a 20:1 ratio requires 500 L/ha of dispersant. Generally only 10 to 20% of this dosage can be delivered, thus thick patches of oil are generally starved of dispersant. This can be overcome by multiple application but at considerable cost.

(b) The tendency of oil slicks to separate into thick and thin patches may result in over- and under-dosing. This is illustrated in Figure 1.1 which is a simulation of the delivery to the 1984 Norwegian W1 test spill as described by Lichtenthaler and Daling (1985). The thin oil received approximately a 1:1 dosage, whereas the thick oil only received a 1:73 dosage. The average dosage was 1:22. It is believed that this type of under-over-dosing phenomenon is quite common.

Figure 1.1

Illustration of over-under-dosing for the 1984 Norwegian W1 experimental spill assuming 400 um diameter dispersant drops.

	THICK SLICK	SHEEN	TOTAL OR AVERAGE
SLICK VOLUME (m3)	9.72	.28	10
SLICK AREA (m2)	4510	27690	32200
SLICK THICKNESS (mm)	2.16	.01	.31
FRACTIONAL AREAS	.14	.86	
DISPERSANT APPLIED (m3)	.133	.311	.444
DISPERSANT FRACTIONS APPLIED	.3	.7	
OIL TO DISPERSANT RATIO	73.0	.89	22.5
NUMBER OF DROPS (MILLIONS)	3977	9279	13256
DROPS PER SQUARE CM	88.2	33.5	41.2
DROP SPACING (mm)	1.06	1.73	1.56
DISPERSANT DOSAGE (L/ha)	295	112	138

(c) The dispersant drop size is often large (eg. 400 um) compared to the thinner parts of the oil slick (eg. 50 um), thus the dispersant drops may break the oil film and induce herding. This will result in much of the oil being unexposed to dispersant. Unfortunately, the larger dispersant drops will fall faster and strike the oil first, resulting in this phenomenon being most prevalent initially.

(d) Although it is relatively easy to calculate dispersant dosage from delivery rate, swath width, and aircraft or boat velocity, in practice there are numerous uncertainties which can combine to create a considerable error in dosage. Uncertainties about oil thickness contribute to an even greater error in the estimated delivered dispersant to oil ratio.

Unfortunately, this delivery factor can only be investigated in expensive full scale tests. It is not amenable to laboratory testing. As has been discussed by Lindblom (1986), it is probably a major reason for poor performance.

Second, the dispersant must mix into the oil, and probably must form a reasonably homogeneous solution. It is suspected that this process is facilitated by having small dispersant drops (with a high area to volume ratio), by matching the viscosities of the oil and dispersant, by there being available sufficient time for this mixing-dissolution process to occur, and by sufficient mixing energy being available. Particularly important are believed to be the relative dimensions of the slick and the dispersant drops and their relative viscosities. If the oil viscosity is large, the dispersant may flow over the oil surface and eventually roll off or wash off. If the dispersant drop viscosity is larger, the drop may retain its integrity as it drops through the slick, and possibly through the oil-water interface into the water. In some cases, we have observed the dispersant to form a layer below the oil, separating the oil and water phases. It is also possible that the dispersant dissolves in the water, establishing a critical micelle concentration, then causing the oil to emulsify, ie. dispersion can be from the water side. In any event, the passage of surfactant to and through the oil-water interface causes intense local turbulence and emulsification. The complexity of these phenomena is discussed in the text by Eicko and Parfitt (1987).

Third is the weathering issue. It has been shown experimentally in laboratory and field that under reasonably energetic conditions 1 volume of dispersant can disperse 50 to 100 volumes of oil provided that it is first well mixed into the oil. This suggests that of the dispersant added initially (eg. 5 parts dispersant per 100 parts oil) much fails to achieve a well mixed condition (eg. of the 5 parts of dispersion delivered to 100 parts of oil, 4 fail to induce dispersion, while 1 part mixes and disperses). Obviously, the chemistries of the oil and dispersant are important variables, as is the oil viscosity. It appears that when the oil viscosity exceeds 5000 cp there is insufficient quantity or quality of energy to shear off the oil droplets. Another complicating factor may be the presence of a rigid oil film adjacent to the interface with water (possibly consisting of asphaltenes and waxes) which is sufficiently rigid to prevent dispersant from migrating to the interface.

It is this third factor which we address in some detail in the remainder of this report. The task is to determine if the oil has weathered to a state such that it has become poorly dispersible or even non-dispersible. It is well established that when oil evaporates to the extent that its viscosity reaches some 5000 cp, it becomes very difficult to disperse. The oil may take up water to form water-in-oil emulsion which further increases the viscosity. These two processes can be quantified by laboratory testing.

The approach taken in this study has been to devise and conduct experiments which have the aim of answering the following questions:

(a) How does a drop of dispersant mix into the oil? Does it flow over the oil, penetrate through it, or mix with it?

(b) How is effectiveness related to dispersant drop size and how does drop size influence mixing?

(c) Is it possible that effectiveness is impeded by a "skin" of precipitated or more hydrophilic material which accumulates in the oil at the oil-water interface and "blocks" access to the dispersant? How can this skin be detected?

(d) Does oil weathering (evaporation) play a more important role than has been previously appreciated? How can this be quantified?

(e) Can an improved dispersion model be developed which is consistent with the observed physical and chemical phenomenon?

2. EXPERIMENTAL

2.1 Materials

The oils used and their properties are described in Table 2.1. The dispersant used was Corexit 9527 obtained from Exxon.

2.2 Dispersion mechanism and mixing tests

The dispersion mechanism was examined using a photographic technique. An Olympus OM-1 was used to photograph the dispersion events which occurred using Corexit 9527 on Beaufort Sea oil.

During the course of the work, we became aware that the physical phenomena are poorly understood which occur when a drop of liquid (eg. dispersant) lands on a second liquid (eg. oil) and falls through it. There is an abundant literature on falling velocities as reviewed by Wallis (1974), but we were unable to find literature addressing the issue of simultaneous falling and dissolution or mixing. For obvious reasons, all reported studies have employed drops of immiscible liquids, such as oil and water. We decided, therefore, to examine the falling/dissolution/mixing behaviour of a liquid in a second mixable liquid. Water-based systems were used in the interest of cost and convenience.

Stock solution of sodium chloride (NaCl), glycerol, and water were prepared and their densities and viscosities determined. NaCl tends to increase density, and glycerol increases viscosity, thus it was possible to prepare liquids of any desired properties. Figures 2.1, 2.2, and 2.3 give plots of density, viscosity, and composition. From Figure 2.3, it is possible to estimate a composition which will yield any desired combination and density and viscosity.

Drops of various diameters were produced by ejection from syringes using needles of various bores, and the falling velocities measured in a vertical column of liquid 5 cm in diameter.

Two novel approaches were used in an attempt to determine the role of possible oil films on dispersion. It is increasingly apparent that when oil weathers, the composition change enhances the precipitation of higher molecular weight chemical species in the oil. Notable are asphaltenes and asphaltene aggregates, resins, and waxes, all of which tend to precipitate at low temperatures. It is also possible that surface active materials present in the oil naturally, or induced by photolysis, accumulate at the oil-water interface and stabilize this film of precipitated material.

The first method involved the use of a viscous traction viscometer which can be used to measure the viscosity at the oil-water interface. The design was based on that described by Davies and Mayers (1960).

Table 2.1 Properties of Oils at 20°C

Oil	Density (g/cm3)	Viscosity (cp)
Beaufort Sea	0.8710	5.93
EPS crude	0.8440	7.09
Alaskan oil	0.8620	9.74

Figure 2.1 Plot of solution density versus composition

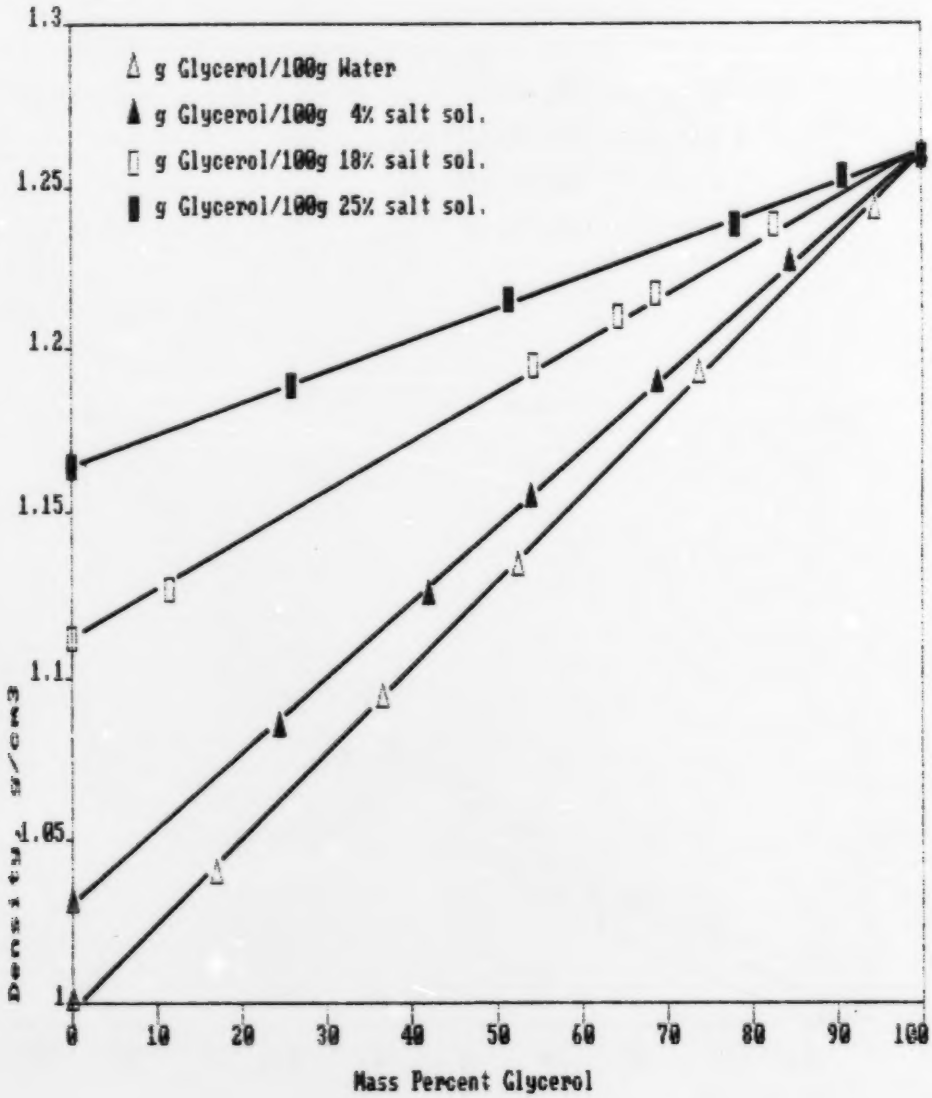


Figure 2.2 Plot of solution viscosity versus composition

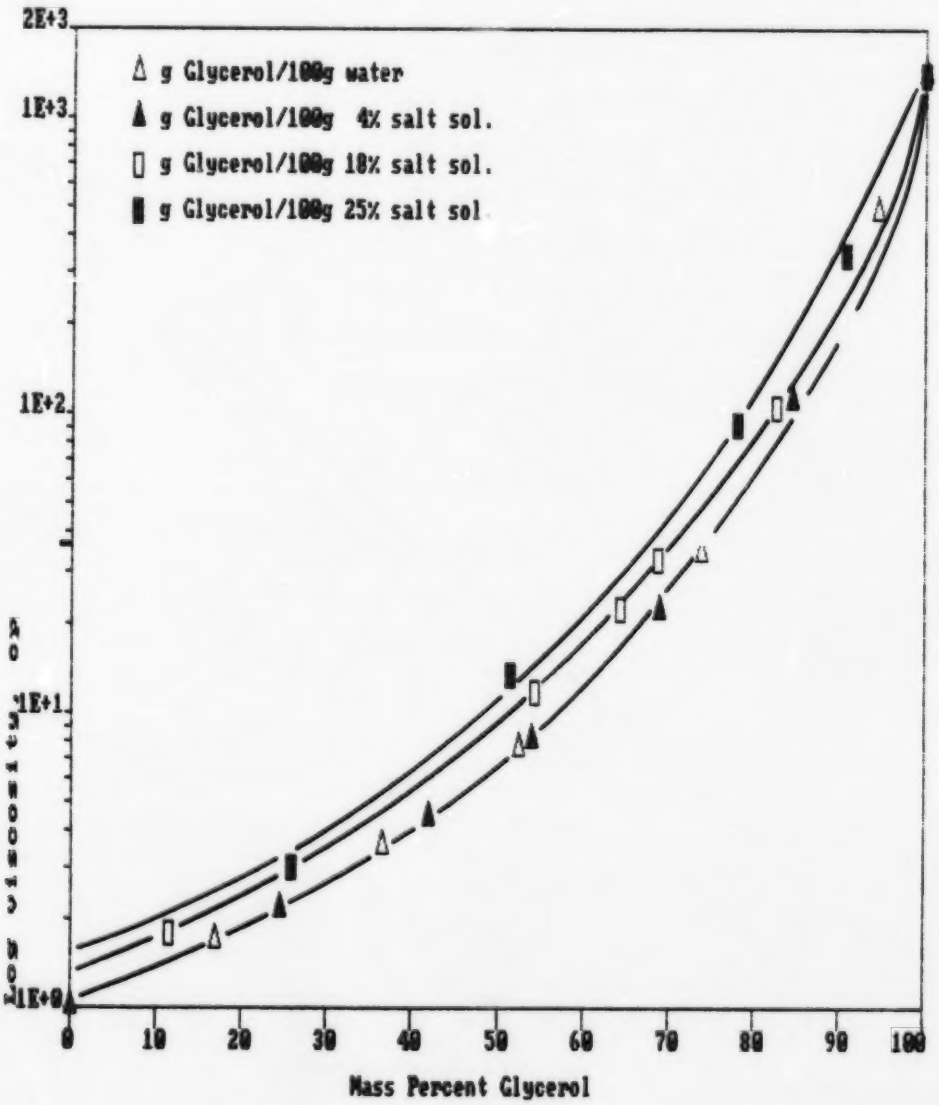
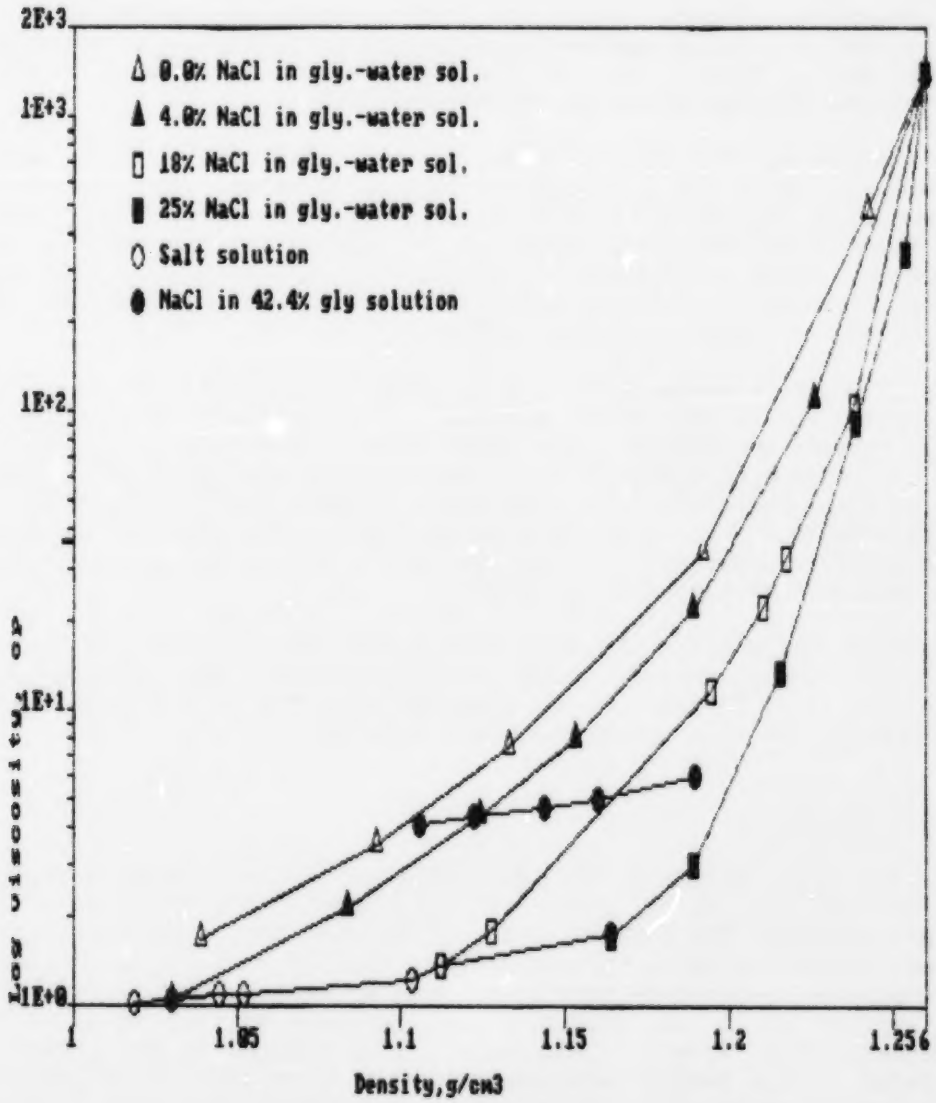


Figure 2.3 Plot of density versus viscosity with composition as parameter



As shown in Figure 2.4, the apparatus consisted of two concentric rings of stainless steel wire (0.064 cm). The diameters of the outer and inner rings were 12.7 cm and 11.2 cm respectively. Support wires were soldered to the rings in such a configuration that the canal formed in between them was of uniform width. The rings were held stationary on the surface, while the liquids rotated in a petri-dish which was 19 cm inside diameter and 10 cm deep, placed on a turntable. The retardation of talc particles sprinkled on to the interface in the canal is a measure of the viscosity of the interfacial layer. Since the hydrodynamics of the process are very complicated, the apparatus is calibrated using liquids of known surface viscosities. Figure 2.5 is the calibration curve based on some film viscosities reported by Davies and Mayers (1960).

At the beginning of a run, the apparatus was calibrated with the air-water surface. A petri-dish was filled with 9 cm of water. Then the rings were lowered on to the surface to form a meniscus in the canal. Talc particles were then sprinkled in the centre of the canal. The turntable was rotated at one revolution in 35 seconds. The revolution time of the talc particle on the clean surface at the centre of the canal was recorded. The average time of one revolution was about 100 s.

To estimate the viscosities at the oil-water interface, crude oil (0.5 mL) was applied on to the water surface. After spreading was completed, the liquid surface was brought again into contact with the canal rings. The talc particles were sprinkled into the centre of the canal. The revolution time with the presence of oil film was recorded. The results are recorded as "retardation", the difference in revolution times of the talc particles on an oil film layer and a clean surface. The interfacial viscosity is then deduced from the calibration curve.

The second and simpler method of testing for the presence of a film was to dip an ice cube in the oil, allow it to equilibrate, then remove the cube. If an oil film formed, it was expected that the film would cling to the ice, whereas the bulk of the oil would flow off.

2.3 Oil Weathering

Two oils (EPS Standard Oil and Alaskan Crude) were weathered by distillation. 250 mL of fresh oil was poured into a 500 ml boiling flask and was weighed. The oil was stirred using a Teflon-coated stirring bar and was heated using a heating jacket. The top part of the boiling flask was insulated to minimize heat loss. During the distillation process, heat was applied at a uniform rate and regulated so that the first drop of condensate fell from the condenser 5-10 minutes after heating was initiated. This temperature was recorded after each 10 ml increment of condensate had been collected in a 100 ml graduated cylinder. Batches of residue (weathered oil) were collected so that the extent of evaporative loss ranged from 10% to 30%. Figure 2.6 shows the distillation curves of the oils.

Figure 2.4 The Schematic Diagram of Viscous Traction Viscometer

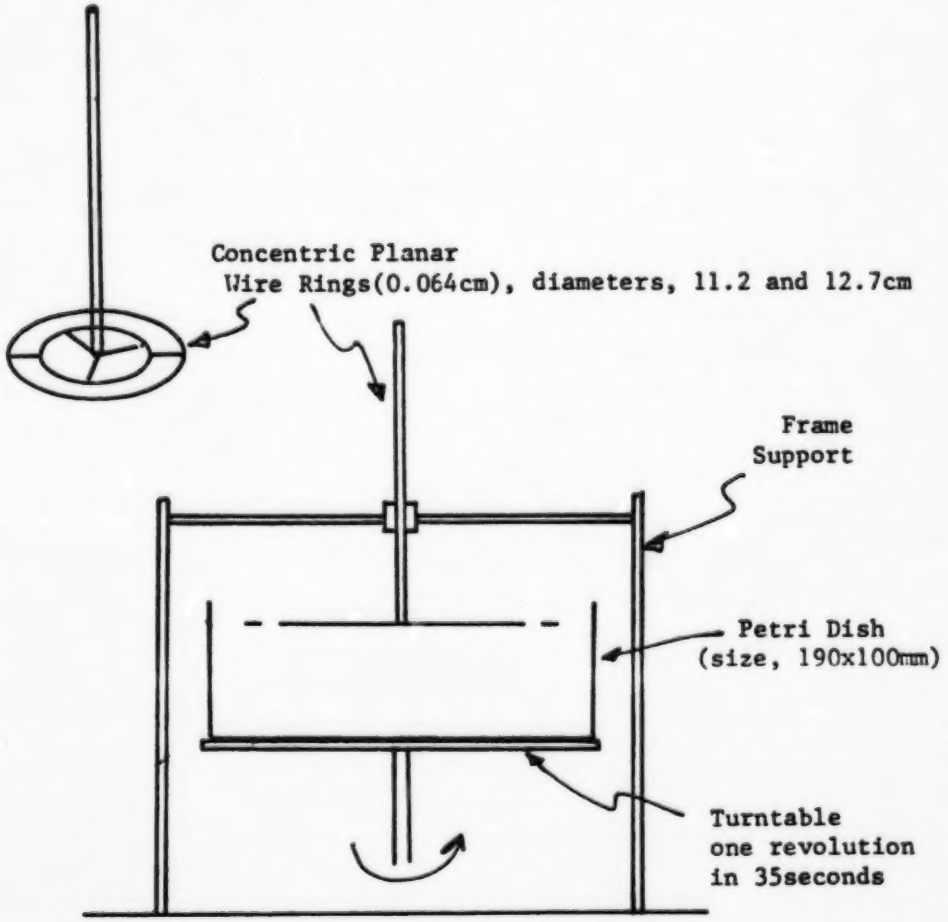


Figure 2.5 Calibration curve as reported by Davies

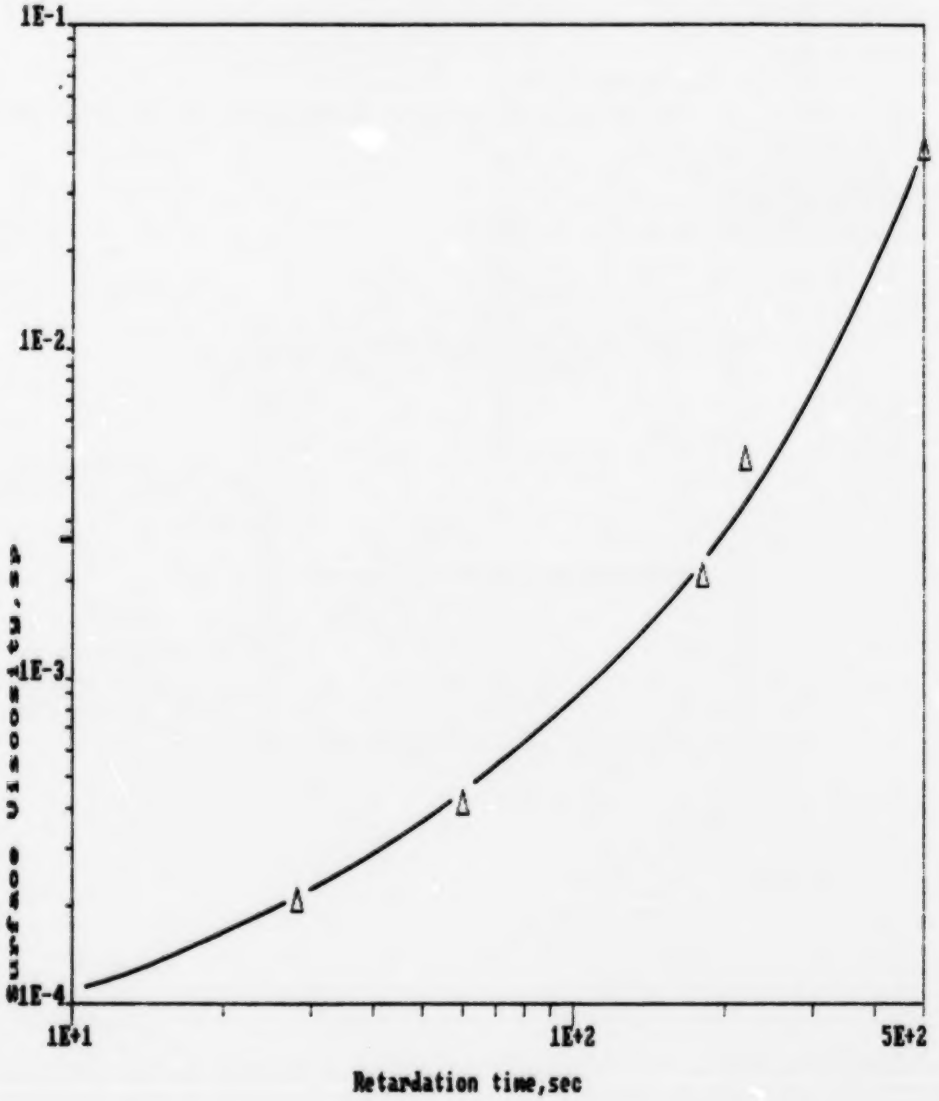
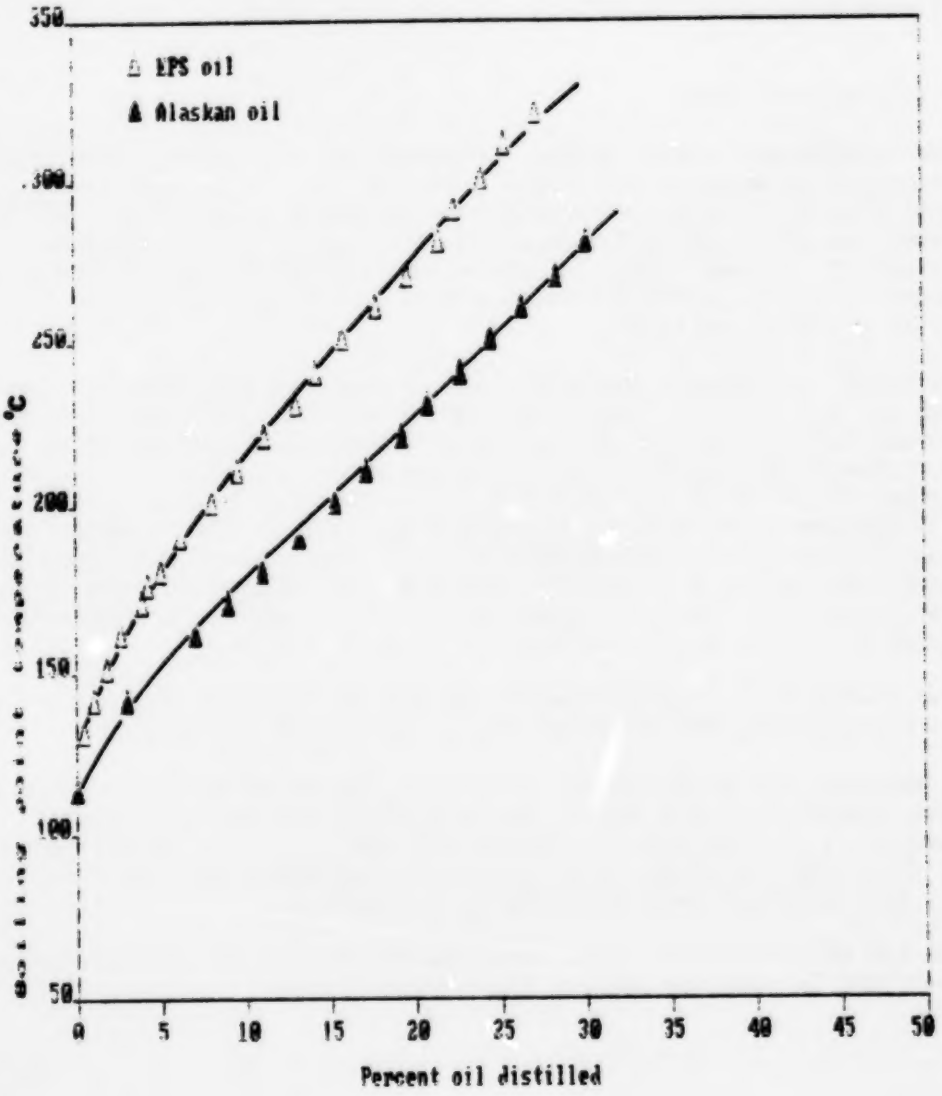


Figure 2.6 Distillation curve of the oils



The weathered oils were stored in a sealed container for later dispersion tests.

Specific gravity and viscosity values were measured for each weathered oil at room temperature of 20°C.

2.4 Dispersion Tests

The dispersion tests where conducted in the Double Tube Apparatus as described by Mackay (1984). For a typical run, salt solution (salinity 33 ppt) flowed through the double tube apparatus at 2.5 L/min, and the water level was set at about 0.5 cm above the top of the inner tube. A known volume of oil was added to the water surface. The dispersant was then added to the oil surface through a nozzle with the tip located at a height of 15 cm above the slick.

In order to control the drop size, a modified dispersant delivery system was devised. This was based on a system used to generate polymer encapsulated insulin-producing cells for in vitro implantation in victims of diabetes and described in a previous report (Chau et al., 1986). The system, illustrated in Figure 2.7, consisted of a syringe pump connected to a dispersant reservoir and a nebulizing unit. The needle was mounted coaxially within a tube through which air was flowed at a controlled rate. By increasing the air flowrate, the drops of dispersant were sheared from the needle at smaller diameter, thus it became possible to generate dispersant drops down to a diameter of about 0.4 mm.

The average drop diameter was determined by counting the number of drops delivered during the discharge of a known volume of dispersant.

To measure the amount of oil dispersed, the inlet and outlet flow of water were clamped shut and the oil was allowed to settle for 2 minutes. A known mass of 2.5 cm-square oil sorbent (3M) was placed on the oil/water surface to determine the amount of oil remaining and dispersed. Allowance was made for the amount of water absorbed by the sorbent.

MNS and WSL dispersion tests were also done using the standard procedure as described in previous reports (Chau et al., 1986).

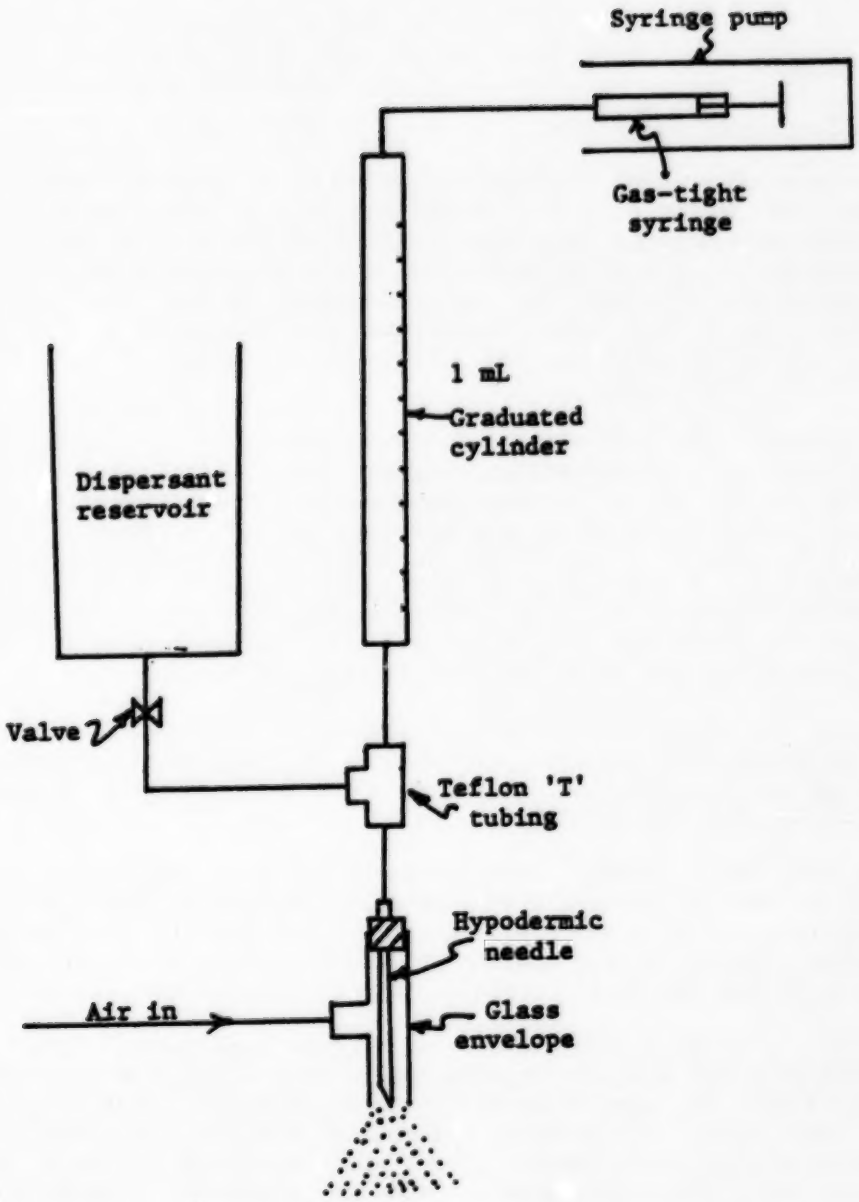


Figure 2.7 The Schematic Diagram of the Spraying Unit

3. RESULTS

3.1 Dispersant-Oil Mixing

The observed results from the mixing tests using water, NaCl, and glycerol are given in Table 3.1. It was striking that despite the fact that both liquids were aqueous and thus easily miscible, the drop retained its integrity for a considerable time, and fell a considerable distance before it broke up. The behaviour was influenced by the relative densities and viscosities of the drops. Surprisingly, the higher the drop viscosity the more rapidly it broke up and dispersed, possibly because it could not circulate internally.

It appears that the dispersant drop lands on the oil surface and tends to penetrate it, accelerating towards (but never reaching) a terminal velocity. If the oil is very viscous, the terminal velocity is so low that the dispersant drop merely spreads over the oil surface. For example, on oils of viscosity approximately 1000 cp, the dispersant drop falling velocity is of the order of 0.05 mm/s, thus it is not likely that the dispersant drop can retain its integrity for long. If penetration does occur, the dispersant drop may tend to disintegrate into smaller drops because of the low oil-dispersant interfacial tension.

If the oil viscosity is low, the dispersant will rapidly penetrate the oil in an intact form and reach the water. This may be the explanation of the maximum in dispersant effectiveness which has been frequently observed, eg. Martinelli and Lynch (1980).

The most rapid breakup occurred with the most viscous drops, suggesting that it may be desirable to use more viscous dispersants or dispersants containing solvents which will evaporate and leave a more viscous residue. A major limitation of dispersant viscosity arises from the need to pump the fluid through the fine dispersing jets in the delivery system.

Figure 3.1 shows one result of the ice cube experiment. The results were encouraging in that it appears that a film was formed and could be easily identified. In order to estimate the strength of this film present between oil and water, interfacial viscosity measurements were taken, using a viscous traction viscometer. The results are given in Table 3.2. It was found that the interfacial viscosity increases considerably when oil becomes weathered. Different oils exhibit a variety strength of the film found. It is believed that any change in surface viscosity may have a significant effect on the oil dispersion process.

Table 3.1 Mixing-Dissolution Results

Bulk phase - Tap water

Composition	S.G.	Drop Viscosity (cp.)	Drop Size (mm)	Avg. Distance to break up (cm)	Avg. Time to break up (sec)	Falling Velocity (cm/sec)
18.1% NaCl	1.1120	1.38	4	7.05	1.35	5.22
			3	6.60	1.30	5.08
			2	5.25	1.15	4.56
25.0% NaCl	1.1642	1.70	4	8.40	1.40	6.00
			3	6.90	1.25	5.52
			2	5.25	1.00	5.25
24.5% wt. Glycerol in 100 mL 4% NaCl solution	1.0837	2.16	4	7.80	1.70	4.59
			3	6.00	1.30	4.62
			2	3.75	1.00	3.75
42% wt. Glycerol in 100 mL 4% NaCl solution	1.1241	4.38	4	6.00	1.50	4.00
			3	4.26	1.15	3.70
			2	2.70	0.80	3.375
54% wt. Glycerol in 100 mL 4% NaCl solution	1.1532	7.98	4	3.30	0.85	3.88
			3	1.80	0.50	3.60
			2	1.50	0.50	3.00
68.8% wt. Glycerol in 100 mL 4% NaCl solution	1.1889	21.7	4	0.75	0.20	3.75
			3	1.05	0.30	3.50
			2	0.90	0.30	3.00
84.4 5 wt. Glycerol in 100 mL 4% NaCl solution	1.2259	109	4	0.30	0.15	2.0
			3	0.60	0.20	3.0
			2	0.60	0.20	3.0

Table 3.1 continued

Bulk phase - Tap water

Composition	S.G.	Viscosity (cp.)	Drop Size (mm)	Avg. Distance to break up (cm)	Avg. Time to break up (sec)	Falling Velocity (cm/sec)
2.5% NaCl	1.016	1.02	4	8.25	3.4	2.42
			3	6.75	2.8	2.41
			2	5.40	2.1	2.57
4.2% NaCl	1.027	1.036	4	6.90	2.0	3.45
			3	6.30	1.9	3.32
			2	4.50	1.5	3.00
6% NaCl	1.038	1.067	4	6.60	1.9	3.47
			3	6.30	1.7	3.70
			2	4.80	1.5	3.20
7.5% NaCl	1.048	1.085	4	6.60	1.6	4.13
			3	6.30	1.6	3.94
			2	4.98	1.3	3.83

Bulk phase - Glycerol/water mixture
S.G. - 1.0955, viscosity - 3.86 cp.

Composition	S.G.	Viscosity (cp.)	Drop Size (mm)	Avg. Distance to break up (cm)	Avg. Time to break up (sec)	Falling Velocity (cm/sec)
18.1% NaCl	1.1120	1.38	4	2.25	2.9	0.78
			3	2.55	2.1	1.21
			2	2.10	0.9	2.33
14.5g Glycerol per 100 mL 18.1% NaCl solution	1.1274	1.79	4	2.25	2.1	1.07
			3	2.40	1.5	1.60
			2	2.10	0.8	2.63
25% NaCl	1.1642	1.70	4	1.50	0.75	2.0
			3	2.40	1.10	2.18
			2	1.50	0.70	2.14
40.8g Glycerol per 100 mL 25% NaCl solution	1.1890	2.98	4	1.20	0.40	3.00
			3	1.50	0.45	3.33
			2	1.65	0.50	3.30

Table 3.1 continued

Effect of bulk viscosity on liquid-liquid mixing

Bulk Phase		Drop(4mm)		Average Distance To	Average Time To	Falling Velocity
Viscosity	S.G.	Viscosity	S.G.	Breakup,cm	Breakup,sec	cm/sec
1.00	1.00	11.7	1.206	2.10	0.70	3.0
1.00	1.00	149	1.250	1.80	0.50	3.6
1.00	1.00	1485	1.258	21.30	3.30	6.5
9.30	1.156	11.7	1.206	3.50	1.80	1.9
9.30	1.156	149	1.250	4.98	2.50	2.0
9.30	1.156	1485	1.258	no breaking up		1.9
99.30	1.230	149	1.250	no breaking up		0.2
99.30	1.230	1485	1.258	Spreading on surface		n/a

Table 3.2 Interfacial viscosity measurement

Oil State	Retardation Times (s)	Surface viscosity (sp)
EPS/Fresh	137	1.4×10^{-3}
EPS/12% weathered	620	8.8×10^{-2}
EPS/27% weathered	780	>0.1
Beauford Sea/Fresh	85	6.6×10^{-4}
Alaskan	1300	>0.1

Figures 3.2 to 3.5 are annotated prints of various stages of a typical dispersion process under static conditions. When the dispersant drop landed on the oil surface, it rapidly penetrated through the oil layer and then became located at the oil-water interface. After a few seconds, the dispersant drop started breaking down and herding the oil. At this time, it is believed that the surfactant components had accumulated at the interface and were actively inducing motion of the neighbouring fluid. It was noted that some of the dispersant was lost into the water column. Regions of oil-water interface were observed to be unstable and subject to emulsification. If no mixing was applied, no oil dispersion could be seen. It appears that some artificial turbulence is needed to enhance the dispersion process.

Figure 3.6 to 3.9 shows the oil-dispersant mixing with air blowing on to the oil surface. The treated oils were dispersed from the surface and formed drops of emulsion which concentrated near the top of the water column.

3.2 Weathering and Effectiveness

Table 3.3 presents the interfacial tension and D50 values (dispersant to oil ratio required to disperse 50% oil) of EPS oil in water using the Double Tube test. The result shows that as oil weathered, the interfacial tension increased and more dispersant was necessary to disperse an appreciable portion of the oil.

Figure 3.10 shows the effect of dispersant drop size on oil dispersion. Small dispersant drops are not so effective on fresh, light oil. It is suspected that much of the dispersant was lost to the water column, hence lowering its effectiveness.
Figure 3.11 presents the effectiveness test results of dispersant applied to various oil thicknesses. It was found that chemical dispersion is favoured on thin slicks. But this situation may not apply at sea because a thin slick is often subject to very rapid composition change as a result of evaporation and thus achieves lower dispersability.

Figure 3.12 and 3.13 present the dispersibility results of EPS oil and Alaskan oil crude at 15°C. It is noteworthy that Corexit 9527 is effective on both oils. As the oils weathered, dispersion became less effective.

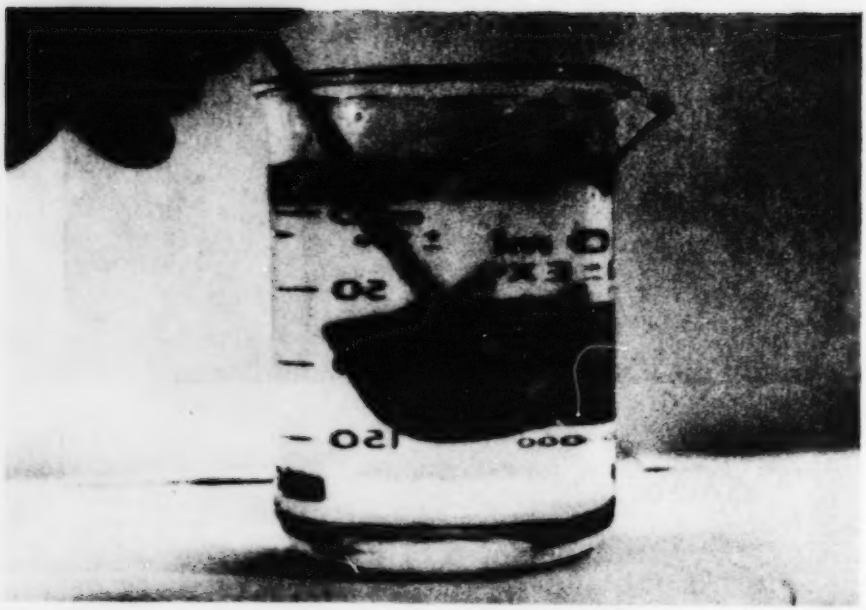


Figure 3.1 Ice cube experiment, showing the oil film formation

Figure 3.2
Dispersant landed on oil surface. (bottom view)

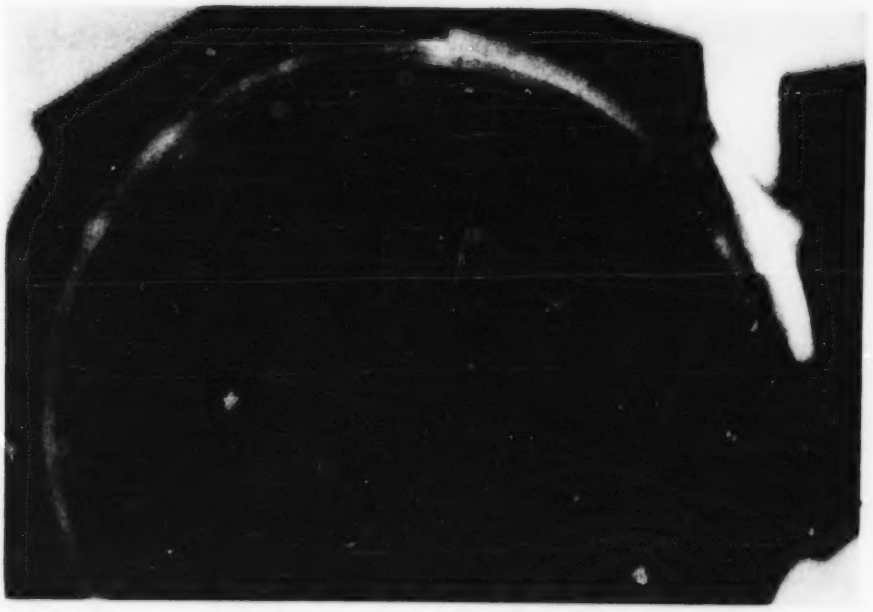


Figure 3.3
Dispersant sank through oil layer, and located at the oil-water interface

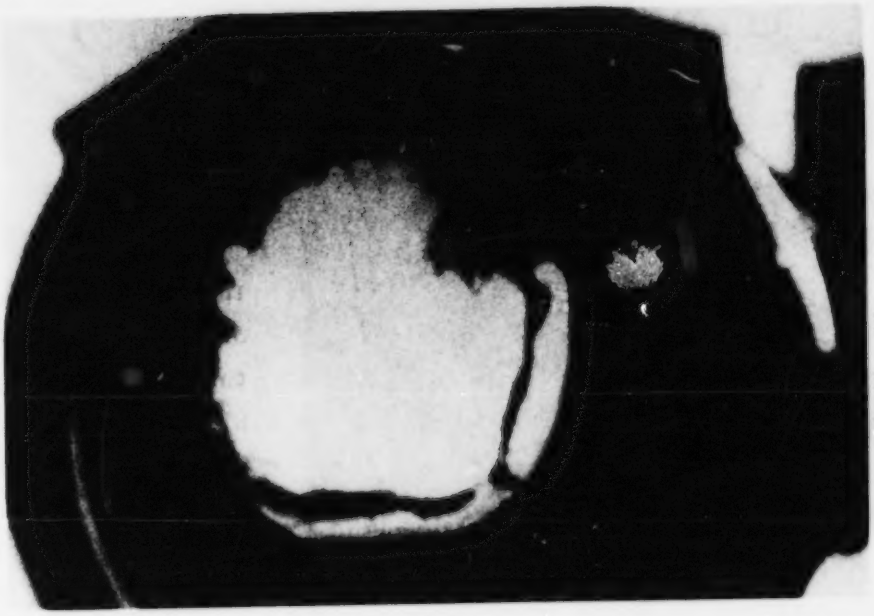


Figure 3.4

Dispersant herding the oil.

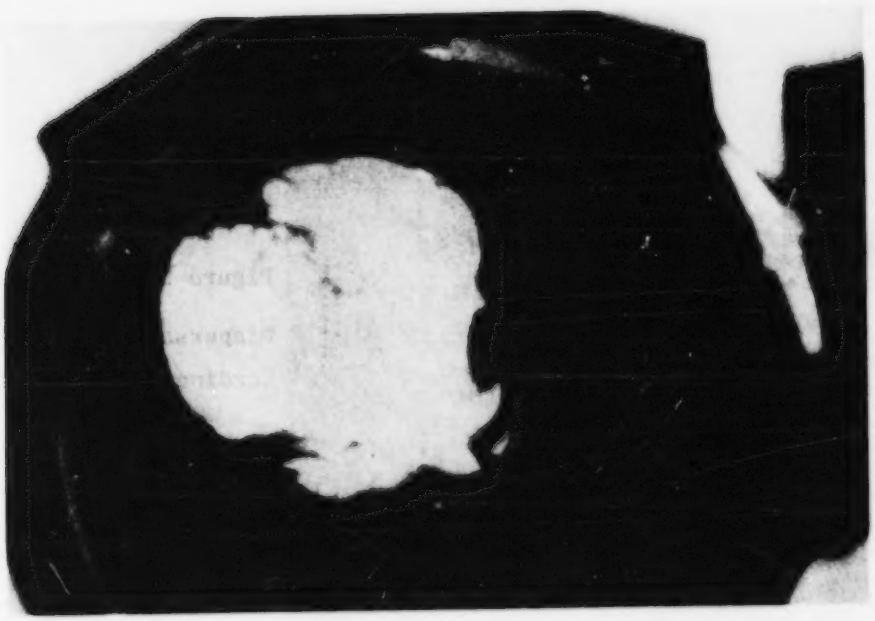


Figure 3.5

Herding continued.

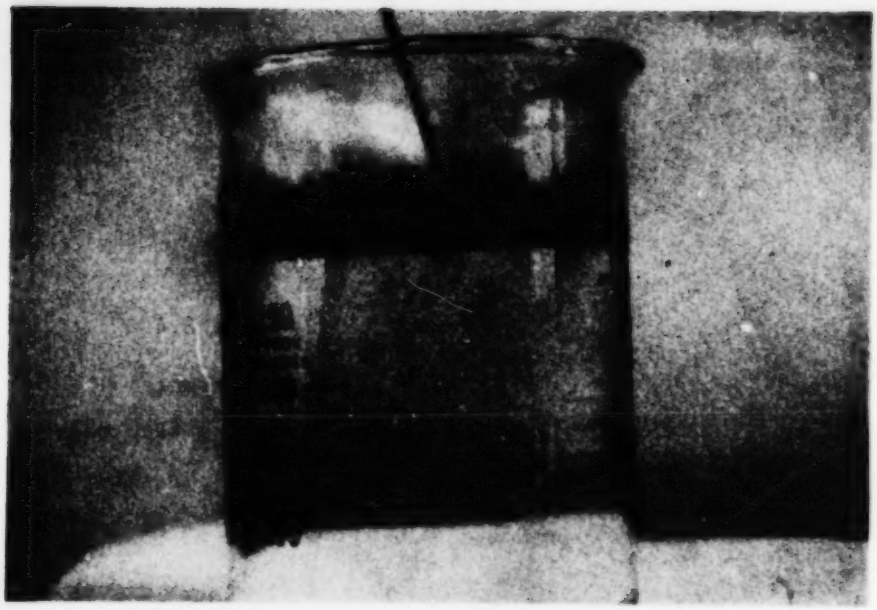


Figure 3.6

Initial oil slick of EPS oil, 0.7mm thickness. (air blowing on to the oil surface)

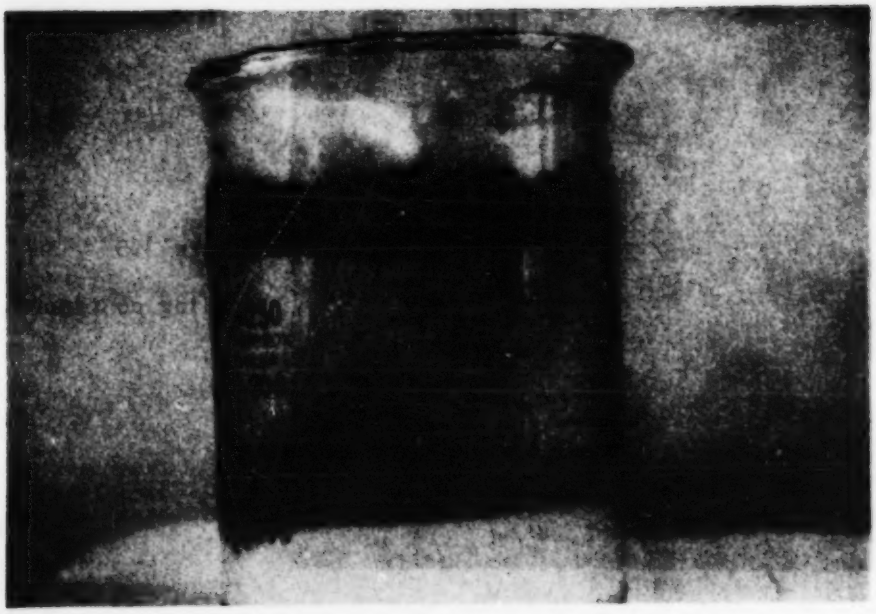


Figure 3.7

Dispersant added, herding occurred.

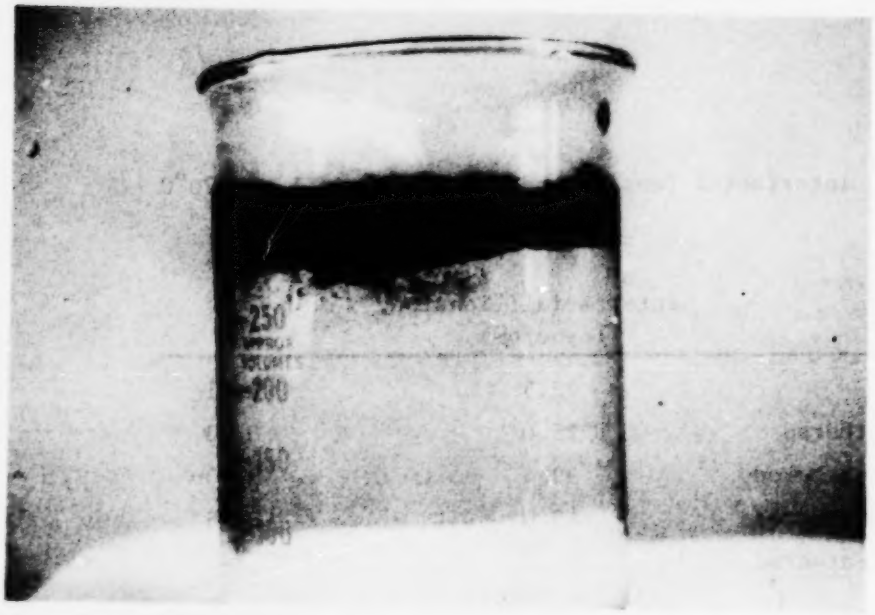


Figure 3.8

Treated oil sheared off from oil-water interface

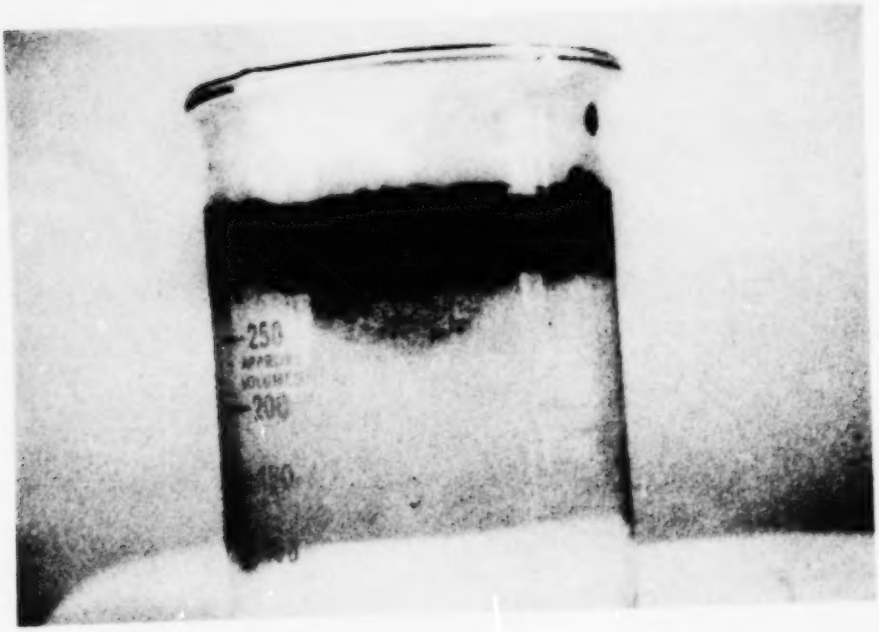


Figure 3.9

Dispersion continued, oil recovered the water surface

Table 3.3 Interfacial Tension and D50 of EPS oil at 20°C

State	Interfacial Tension (dyne/cm)	D50
Fresh	22.5	0.01
12% weathered	25.0	0.03
19.2% weathered	39.4	0.036
27.0% weathered	43.0	0.05
33.4% weathered	47.2	-

Figure 3.10 The Effect of Dispersant Drop Size on Dispersion

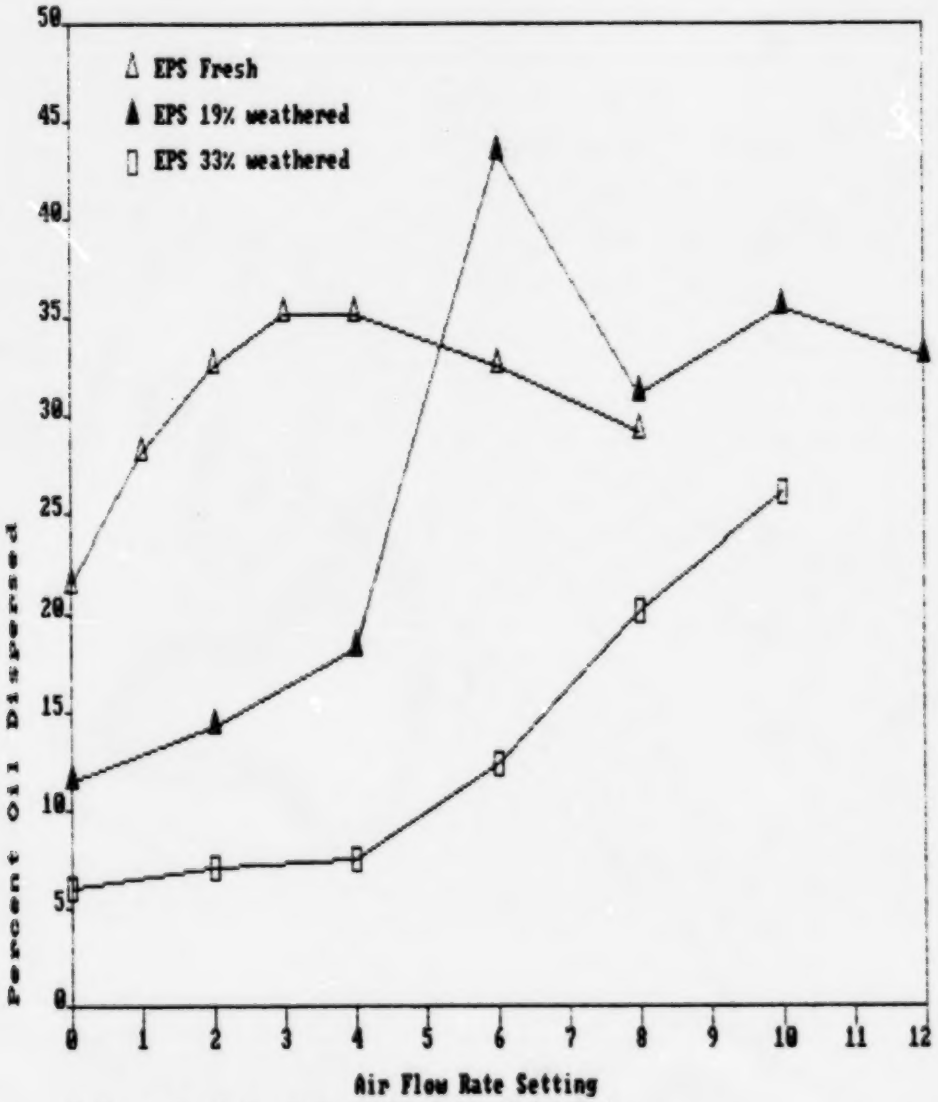


Figure 3.11 The Dependence of Dispersion on Slick Thickness

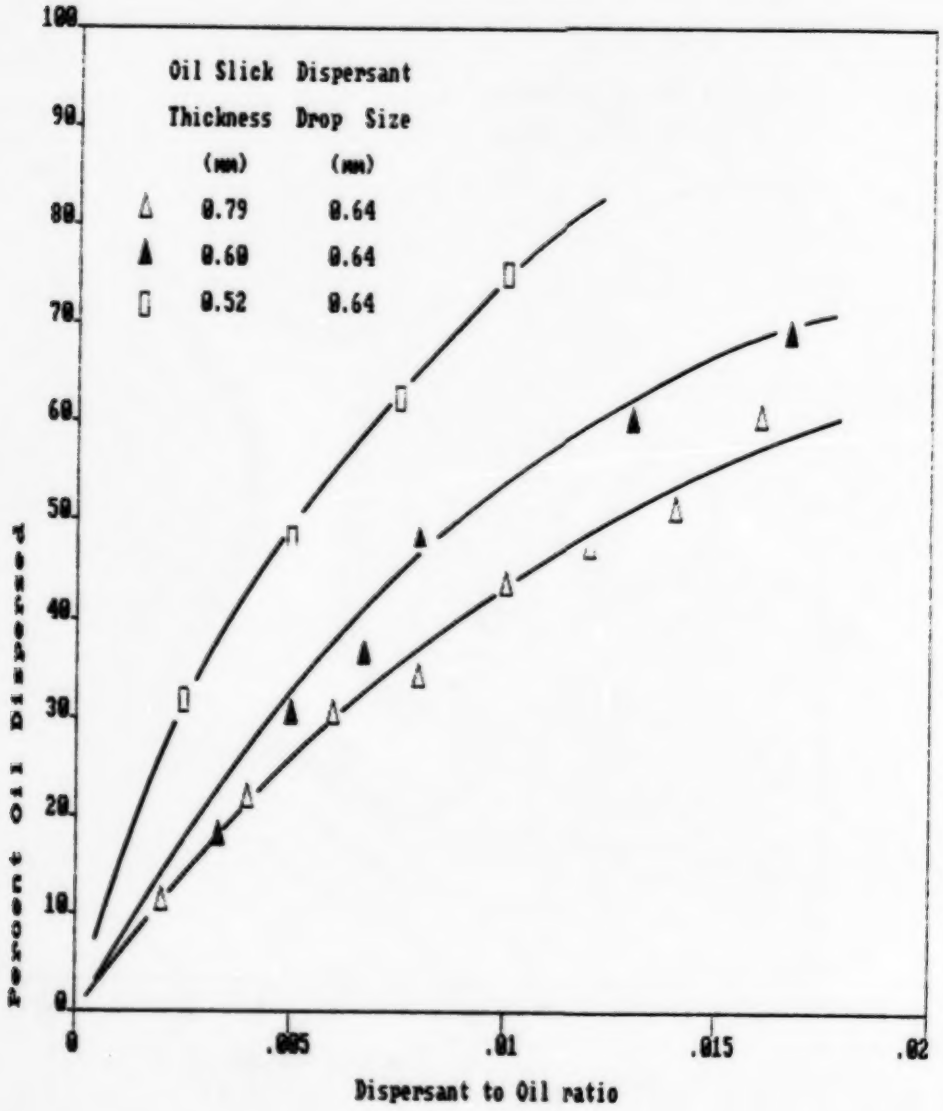


Figure 3.12 Dispersion Test of EPS oil with Corexit 9527

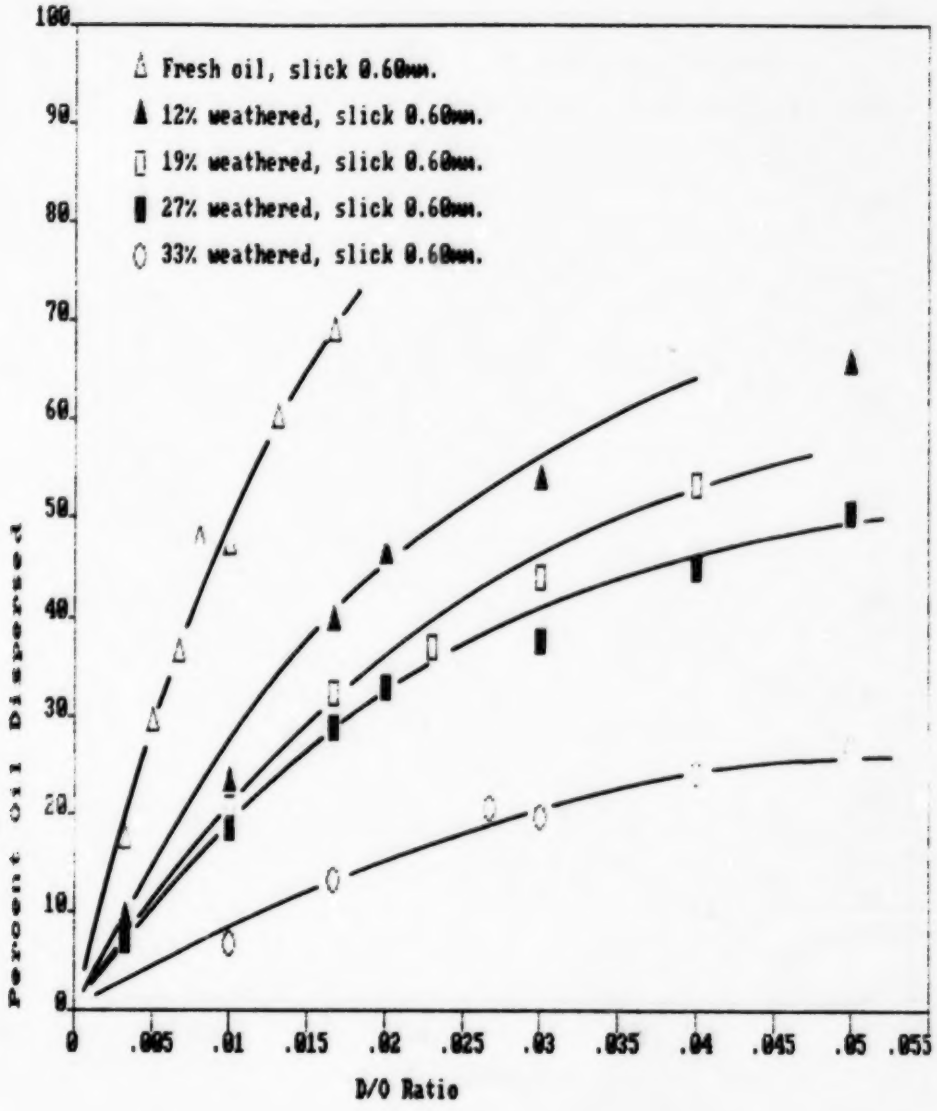


Figure 3.13 Dispersion Test of Alaskan Crude Oil with Corexit 9527

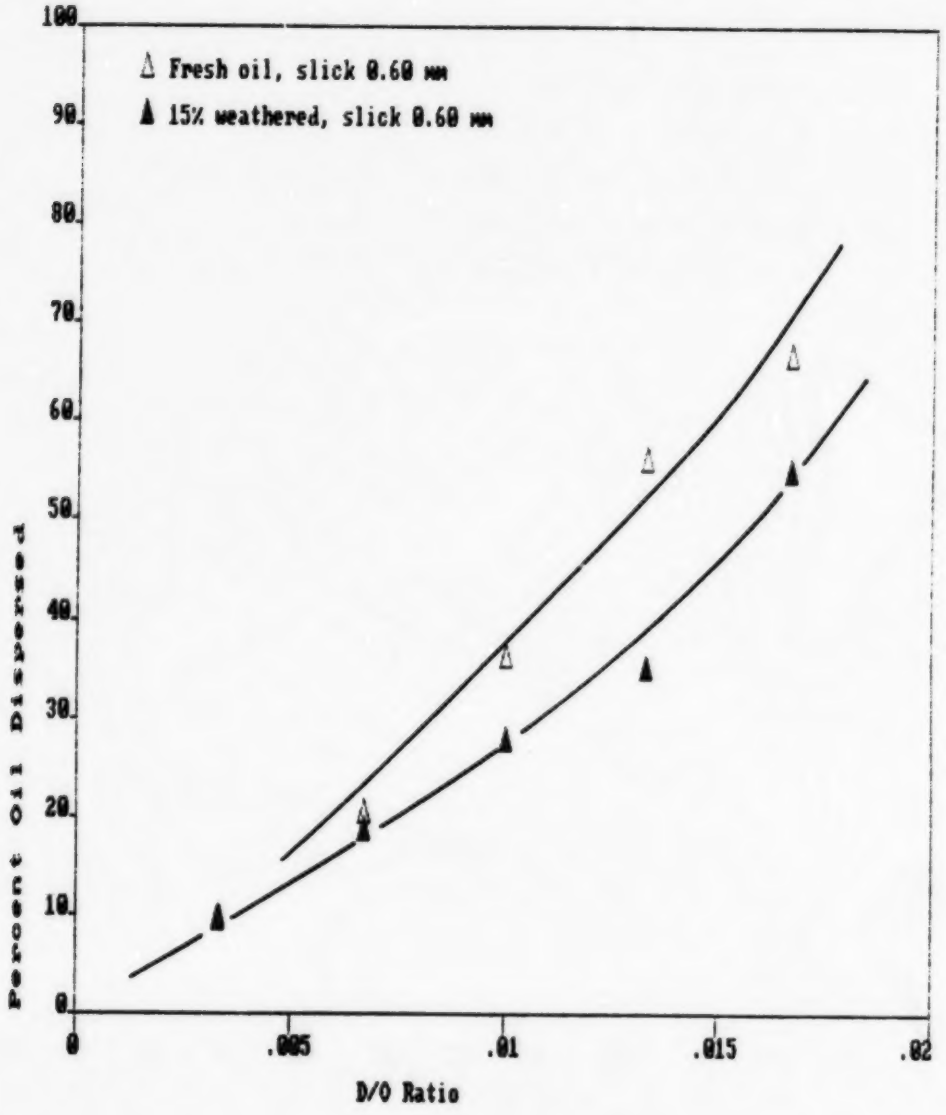


Table 3.4 The dispersion test of EPS oil, using the MNS Apparatus

Oil/State	Evaporative Explosure, E	Water Temperature (°C)	Density g/cm3	Viscosity cp	Percent Oil Dispersed Dispersant to Oil Ratio 0.015	0.020	0.025	0.030
EPS/fresh	0	20	0.3440	7.09	55.0	67.4	-	-
		15	0.8460	9.10	33.0	42.7	58.0	-
		7	0.8500	12.60	23.2	30.1	41.0	46.7
EPS/12%W.	1517	20	0.8650	12.50	49.4	54.8	-	-
		15	0.8720	20.50	32.0	45.3	52.7	-
		7	0.8750	33.30	14.4	19.7	31.3	36.6
EPS/19%W.	11556	20	0.8740	19.80	35.0	44.8	52.6	-
		15	0.8875	36.40	23.2	34.7	42.9	39.7
		7	0.8940	105.70	16.3	18.9	26.4	-
EPS/27%W.	114344	20	0.8860	40.14	23.3	26.1	26.8	33.0
		15	0.9060	87.00	15.4	19.0	21.9	23.5
		7	0.9120	1040.00	10.1	15.1	-	-
EPS/40%W.	4710956	20	0.9070	170.00	9.1	10.2	-	13.1
		15	0.9120	380.00	2.5	5.0	-	-
		7	0.9180	16800.00	1.2	3.1	-	-

Figure 3.14 Result of Labofina Tests With EPS Oil & Corexit 9527

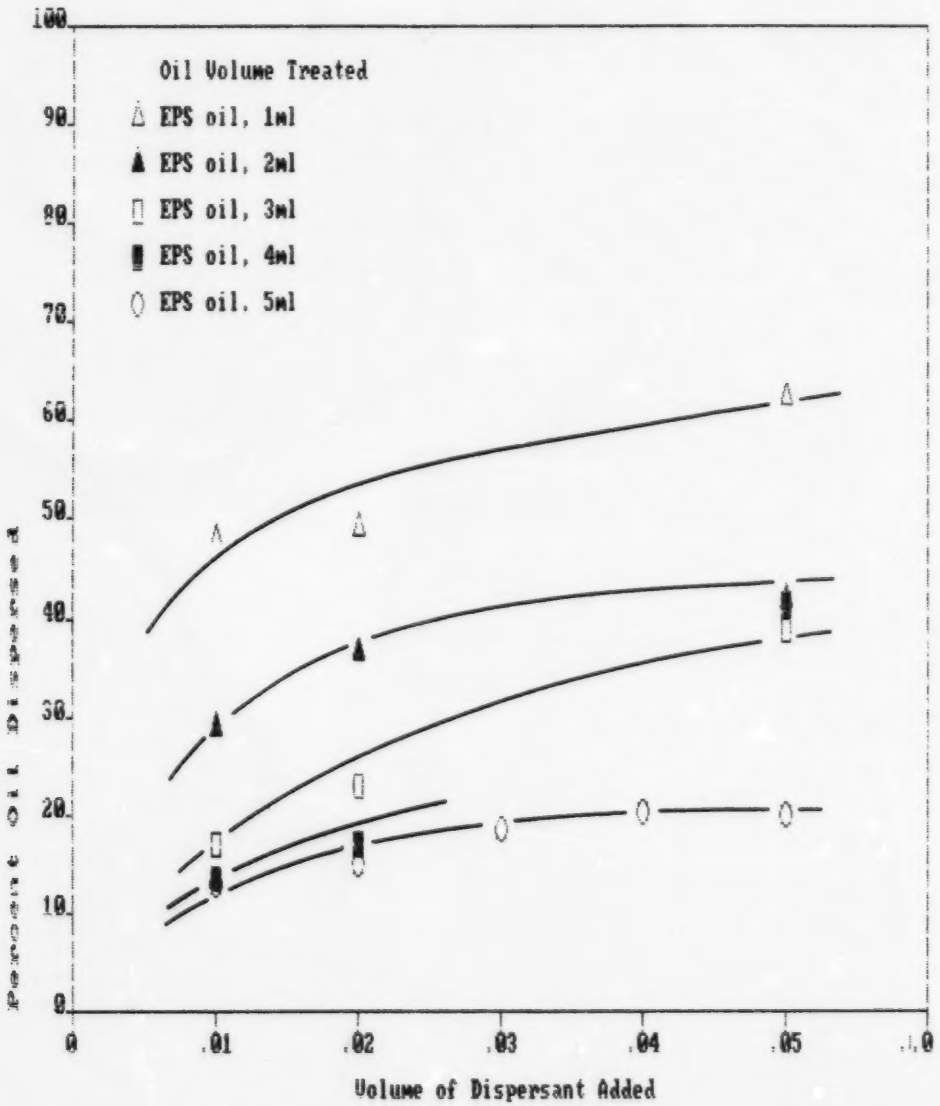


Table 3.4 shows the dispersion test results on EPS oil using the MNS Apparatus. Again, as oil weathered and increased in viscosity, dispersion became difficult.

Figure 3.14 presents results from the dispersion test of EPS oil using the Labofina Apparatus. The results indicate that the stability of oil dispersion increases with increasing dosage of dispersant. Most of the dispersed oil is achieved by the first unit of dispersant that mixed with the oil. These results are the subject of more detailed interpretation later.

4. DISCUSSION

4.1 Mixing

It had been hoped that the mixing tests would yield an equation or model describing the fraction of a dispersant drop which is retained in the oil or sufficiently close to it to cause dispersion. That fraction (F) is presumably related to the variables:

* dispersant drop size
* dispersant drop viscosity
* dispersant drop density
* oil viscosity
* oil density
* oil thickness
* dispersant drop terminal velocity

We are unable to write such an equation because the roles of some key variable are not yet clear.

The results indicate that a high value of F is usually promoted by

* small dispersant drop size
* large oil viscosity

The effects of the other variables are not clear. Particularly puzzling is the effect that thinner oil slicks are more easily dispersed. It had been thought that the opposite would occur.

Consideration of these results and others reported in the dispersant literature leads to the conclusion that the mixing process of a dispersant drop on an oil film on water is an intensely complex process. The process is highly dynamic, involving the dissipation of the drop's kinetic energy, deformation of the drop and the oil with substantial forces being induced by the surfactants as they modify the interfacial tensions between air, oil, water, and dispersant. It is probably impossible to describe this process mathematically. The best that can be hoped for is a set of empirical "rules" or "observations" of the type "the dispersant drops are most effective if in the 200 to 400 um range" which are broadly supportable by insights into the nature of the dispersion process.

Even if the process could be better understood, it is unlikely that much could be done in a countermeasures context to change the variables for the better. No real control can be exerted on the oil and the dispersant drop properties are forstrained by delivery considerations. While mixing is still believed to be an important determinant of effectiveness, there is little that can be done to enhance better mixing. The aim should be to avoid conditions of obviously poor mixing.

4.2 Inherent Dispersibality

In previous studies, we have suggested that, provided that there is sufficient oil available, the "captured" dispersant is capable of dispersing perhaps 50 time its volume of fresh oil. This performance factor (N) of 50 probably falls as the oil becomes very viscous and if a film precipitates at the oil-water interface. A key capability would be to relate this quantity to the extent of weathering but to do this requires that the extent of weathering be quantified. This issue is addressed later.

The performance factor N is also profoundly influenced by the extent of turbulence at the oil-water interface as quantified, for example, by sea state.

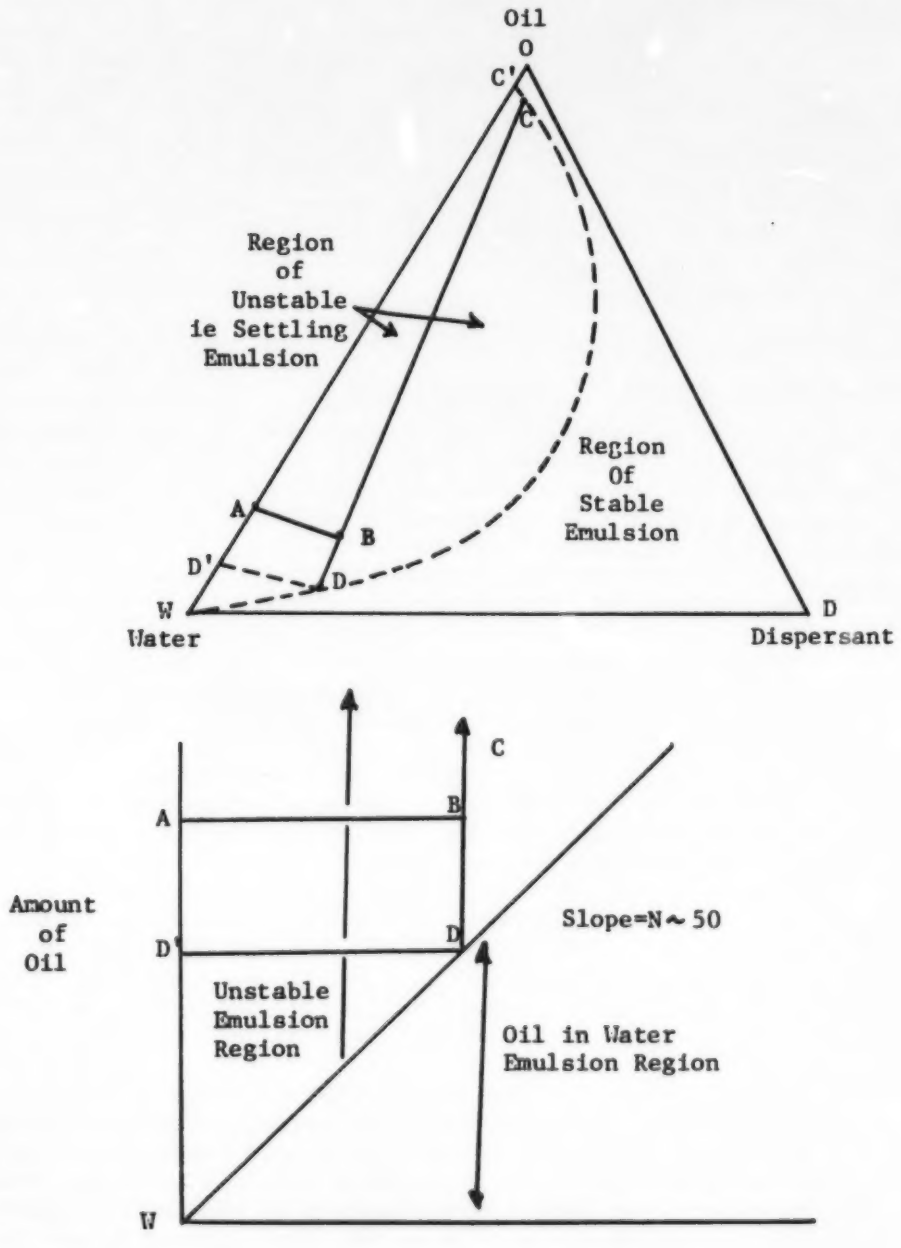
We believe that the laboratory tests, such as MNS or WSL, give a fair indication of this dispersability. ALthough the tests are fairly repeatable, they measure different phenomena, and only broad similarity in results is expected. It is unrealistic to expect them to rank dispersants in exactly the same order. The best that can be hoped for is a broad discrimination between the best and worst performing products. The results obtained in this study suggest that surface viscosity and the presence of a precipitated oil film may be important variables controlling N. Unfortunately, it is very difficult to investigate these films.

A thoughtful examination of these results suggests that when interpreting the dispersability phenomena, something is being missed, or the data are being viewed in a misleading context. It is rather analogous to the early difficulties in interpreting planetary orbits, in which the assumption had always been made that the planets revolve around the Earth. Realization that the planets and the Earth revolve around the sun greatly simplified and clarified astronomical thinking. Perhaps there is a similar realization to be gained by examining the dispersion data in a different light. One approach is considered below.

In the surfactant literature, frequent use is made of triangular diagrams, as illustrated in Figure 4.1. The apices correspond in this case to pure dispersant, oil, and water, the sides as binary mixtures, and the interior as tertiary mixtures. Such diagrams are frequently used in the solvent extraction literature when treating solvent-solute-diluent equilibria.

Untreated oil-water mixtures lie generally in the vicinity of the point A on Figure 4.1, consisting of water and oil in an effective ratio of perhaps 100 to 1. The oil and water are essentially unmiscible, thus the oil-water side represents a two phase region, except at the very apices corresponding to the solubility of oil in water (approximately 30 ppm) and of water in oil (perhaps 1000 ppm). As dispersant is added, the mixture moves to B. The distance is exaggerated for clarity. The mixture B then separates into C and D. C is undispersed oil (possibly containing some water and dispersant), and D is emulsion of oil in water with dispersant. Using the lever rule, the ratio BD/BC is the ratio of the volumes of undispersed oil to emulsion and is normally very small.

Figure 4.1 Schematic Triangular and XY Diagrams Depicting the Dispersion Process



Projection of C and D back to the oil-water side (which is equivalent to ignoring the dispersant) gives two new pseudo phases, C' and D', representing respectively undispersed oil and dispersed oil. If the oil is totally dispersed, the point D' and A will coincide, ie., the original oil-water mixture is now emulsion. At zero dispersion, D' coincides with the water apex. The location of D' along the line WA thus is a measure of the effectiveness, in fact the effectiveness expressed as a fraction is approximately D'W/AW.

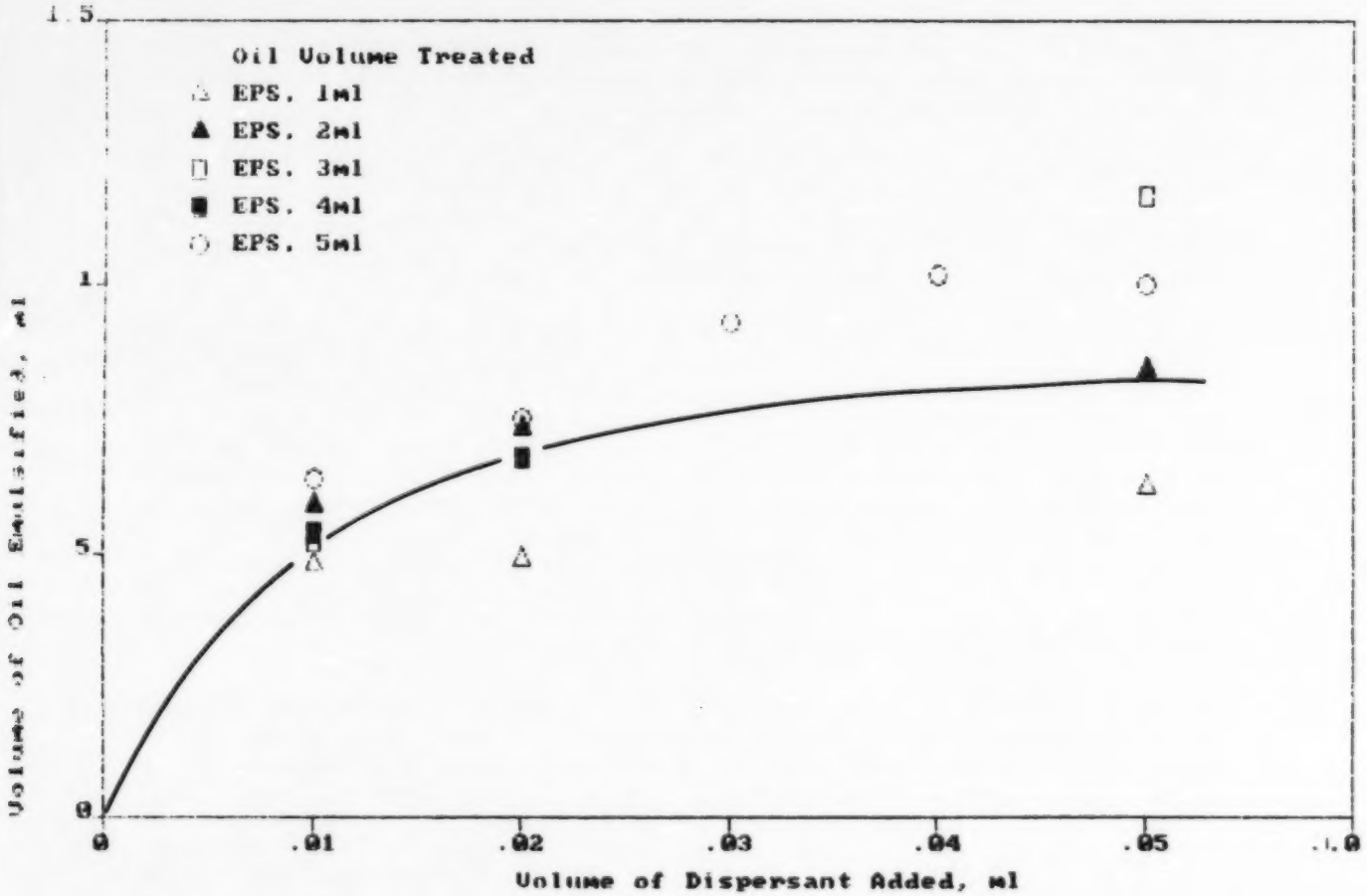
The key property of this diagram is thus the location of the line WD, which expresses the extent to which the addition of the surfactant enhances the ability of the water to contain emulsified oil. A steep slope is desirable. The factor N described earlier is essentially this slope. Unfortunately, the evidence points to this line being sensitive to the degree of turbulence present, thus the diagram is not purely thermodynamic in nature - it is also kinetic.

Unfortunately, it is not feasible to plot dispersion results on a simple triangular diagram, because most of the points are squeezed into the bottom left apex. This region can be "blown up" and represented on conventional graph paper by plotting oil concentration on the y axis versus dispersant concentration on the x axis, as also shown in Figure 4.1.

The dispersion process is now A to B to D, and the effectiveness is again D'W/AW, and the slope is N. The data in Figure 3.14, which are from the Labofina tests, can be replotted in this format in Figure 4.2 as volume of oil emulsified versus volume of dispersant added. The data suggest that the addition of 0.01 mL dispersant causes emulsification of 0.5 mL oil, ie., N is 50, but addition of more dispersant does not continue to increase the volume of oil emulsified at this rate. The line "levels off". An interpretation of this is that a type of "oil emulsion solubility limit in water" is reached. The volume of water in this test system is constant at 250 mL, thus it appears this "solubility limit" is in the region of 1 mL oil per 250 mL water or 0.4%. Water seems to be unable to accommodate emulsions which are more concentrated than this.

If this argument is accepted (and it should not at this stage be regarded as being proved), then certain implications follow. When dispersant is added to oil under conditions in which the volume of accessible water is large, each volume of dispersant will emulsify 50 volumes (approximately) of oil. But if volume of accessible water is smaller, emulsification can only proceed to give a maximum emulsion concentration of about 0.4%. Adding more dispersant has no beneficial effect. The MNS apparatus always operates well below this concentration, and the Labofina apparatus often above it, thus differences in dispersant ranking between these systems may reflect this effect.

Figure 4.2 Labofina Test Results (Fig. 3.14) Plotted in a Form Simular To Fig.4.1



At sea, with a 1 mm thick slick, achievement of a 0.4% concentration corresponds to a water depth of 250 mm or 25 cm. During the dispersion event, it is thus imperative that the emulsion formed under the slick is removed by turbulent eddies and replaced by fresh water. If there is limited removal, there will be limited dispersion. This suggests a re-examination of the role of oceanic turbulence or sea state. It has always been assumed that turbulence contributes to dispersion only by providing better shearing of the oil from the water. As important may be its role in removing emulsion from the vicinity of the slick. It seems possible that some of the well documented failures to disperse oil at sea corresponded to conditions in which the water under the slick was poorly mixed vertically. If this is the case, it should be possible to devise a simple "at sea" test to characterize vertical diffusion, by for example, dropping dye on the water surface and observing its disappearance.

Perhaps one of the difficulties in interpreting the mass of dispersion data which has been generated over the last decade is that we have ignored the capacity of the water to accept or accommodate emulsified oil. We raise this possibility here in the hope that it may receive more investigation in the future.

4.3 Weathering

In the oil pollution literature, several criteria of weathering have been used, namely

* volume fraction of oil evaporated
* mass fraction of oil evaporated
* distillation temperature
* time of exposure to evaporation
* evaporative exposure

We prefer the use of dimensionless evaporative exposure E as defined by Stiver and Mackay (1984). It can be defined as either KAt/V or Gt/V where K is an evaporation mass transfer coefficient (m/h), A is the oil area (m^3) and G is flowrate of gas (m^3/h) which may be sparged through the oil and becomes saturated with oil vapour. The first definition is most convenient when the oil is evaporated from a tray with a wind stream, and the second when gas sparging or bubbling is used. E is an accurate determinant of extent of evaporation at a specified temperature and can be readily converted to a time if K, A, and V are known. V/A is of course Z the initial oil thickness. Time alone is not a meaningful criterion since the extent of evaporation is sensitive to oil thickness. If time is used, thickness and K must also be specified.

E can be related to F, the volume fraction of oil evaporated by the equation

$$F = (1/Q \ln (1 + H_O Q E)$$

where $Q = 10.3\ T_G/T$

and $H_O = 6.3 - 10.3\ T_O/T$

and T is the environmental temperature (K), T_O is the oil's initial boiling point (K), and T_G is the gradient of the boiling point vs F line (K). The constants 6.3 and 10.3 were fitted by Stiver and Mackay (1984) from experimental data for five crude oils.

F can be related to T_B by the simpler linear equation

$$T_B = T_O + FT_G$$

It is also possible by substitution to relate E to T_B.

We prefer to use E as a criterion of weathering since it is easily related to time, F, and hence T_B. Often in experimental studies the oil is "topped" to a specific value of T_B.

If the spill is of constant area, E is simply KAt/V or Kt/Z. If A varies with time, ie. the spill spreads, then the time dependence must be included. Often A varies with $t^{1.5}$ thus we can write

$$A = kt^{1.5}$$
$$E = KA/Vdt = Kkt^{1.5}/Vdt = Kkt^{2.5}/(2.5V)$$

It is striking that E now varies with the t to the large power of 2.5, thus in equal time increments 1, 2, 3, 4, 5, E will vary in the proportions 1, 5.6, 15.6, 32, 56, ie. it increases very rapidly. The reason for this is that as the slick thins, its area/volume ratio increases resulting in faster evaporation. It is often not appreciated that very thin slicks are subject to very rapid composition change as a result of evaporation. If, for example, a 1 cm layer of oil loses 10% by evaporation after 10 hours, then a 1 mm slick will lose 10% in 1 hour, and a 0.1 mm slick 10% in 6 minutes and a sheen of 0.01 mm or 10 um will require only 36 seconds. It follows that we can expect thin parts of a slick to be very extensively weathered.

It is relatively straightforward to measure the dependence of oil density, viscosity, and pour point as a function of E. The most convenient method is to distill the oil to a specified extent of evaporation. If desired, the oil can be distilled into several fractions, then the original oil and various weathered oils reconstituted by adding back the distillates sequentially to the residue. Samples can also be subjected to GC analysis to provide a record of oil composition. These samples can be used to "match" environmental samples and thus determine their evaporative state or history. It may be convenient to regress these properties as a function of temperature and E.

Using a laboratory test such as the MNS, Double Tube, WSL/IVL, or IFP procedures it is possible to determine the dependence of dispersability on extent of evaporation. There are two general approaches.

If a dispersant to oil ratio (DOR) is specified of say 1:50, the dispersion efficiency can be measured and plotted against E. Alternately, test DOR values can be sought which yield about 50% dispersion and the volume of oil (N) dispersed per unit volume of dispersant is then calculated. Usually N decreases as the oil evaporates and becomes more viscous. N usually approaches low and uneconomic values when the oil reaches a viscosity of several thousand centipoise.

The advantage of the latter "50% dispersion" approach is that it better separates or "spreads out" the performance of different dispersants. The use of a fixed DOR may result in all the high performance products giving effectiveness figures in the 85 to 100% range with inadequate discrimination. In principle, the 50% approach is similar to the search for a lethal concentration to 50% of the test organisms in an aquatic bioassay.

It is also possible to test the emulsion (mousse) formation tendency of the weathered oils by a standard shaking-settling procedure and determine the dispersability of the resulting emulsions. An illustrative plot of N versus E for fresh and emulsified oil is given in Figure 4.3.

A complete picture of the oil's dispersability can now be obtained by compiling all these data in the form illustrated in Figure 4.4. The oil properties and dispersability data apply at a specified temperature. If the area-time histories of thick and thin parts of the oil slick are known, it becomes possible to include time scales using the appropriate relationships between E and time.

In bringing together all the weathering factors, this figure highlights two problems which correspond to the opening and closing of dispersant application "time windows".

At short exposure times, it may not be feasible to disperse the oil because the response time is not adequate. Further, the thick oil (eg. greater than 1 mm) requires, at least in principle, a dosage of approximately 500 L/ha which may be too large to be feasible. Lower dosages could be applied and probably would have some desirable effect, but the risk remains of underdosing this thick oil. This thick oil, which is relatively small in area, may also be difficult to target.

For these reasons, it may be difficult to apply dispersant effectively to the area to the left of Figure 4.4, ie. it is a region in which the time window has not yet opened.

A more serious problem arises to the right of Figure 4.4 when the time window closes. A point (with a specified E) will be reached at which the oil viscosity is too high and an excessive amount of dispersant (N) must be added, to achieve reasonable dispersion. The problem may be related to the oil's chemistry, viscosity, pour point, or susceptibility to emulsion formation. If this E can be identified, the corresponding times can be deduced and the time of "closure of the dispersion time window" determined. It is suspected that for some oils which spread and evaporate rapidly to

Figure 4.3 Plot of Dispersability as a Function of Evaporative Exposure

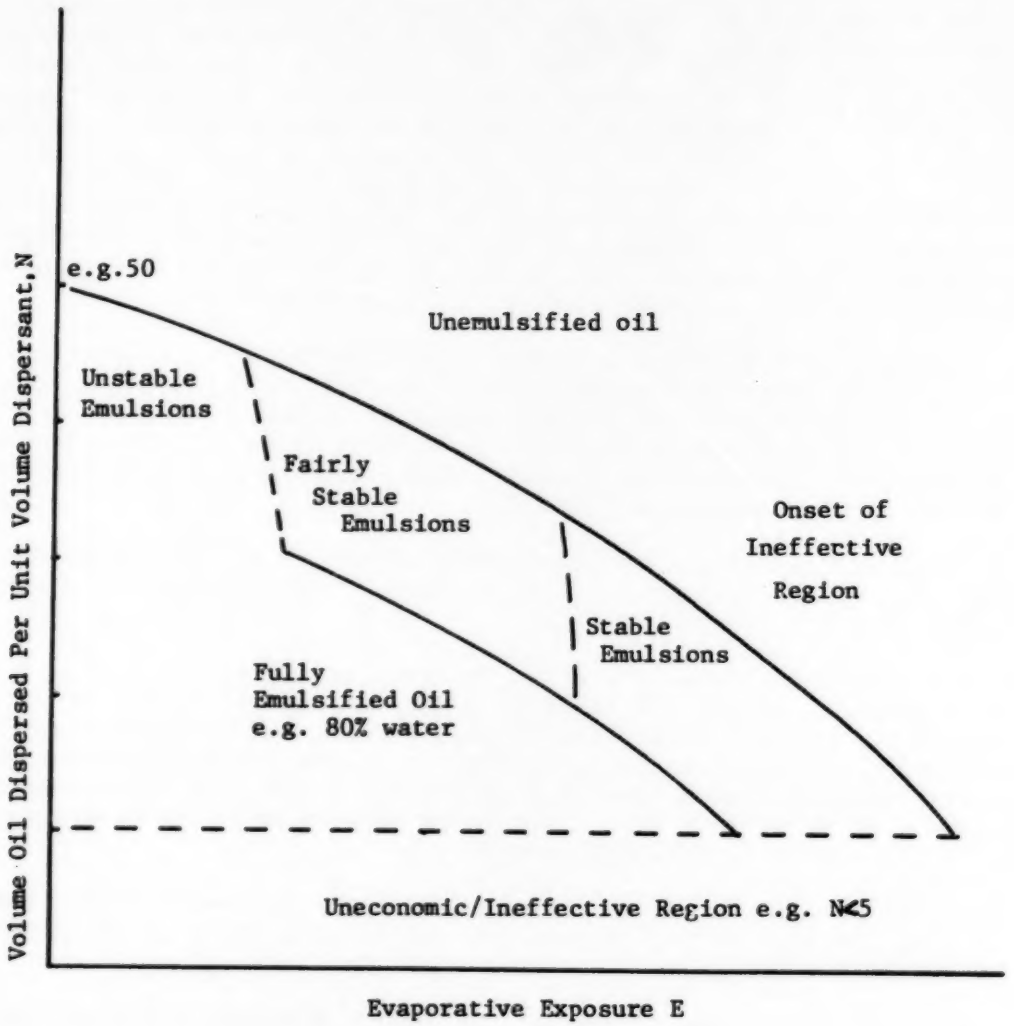
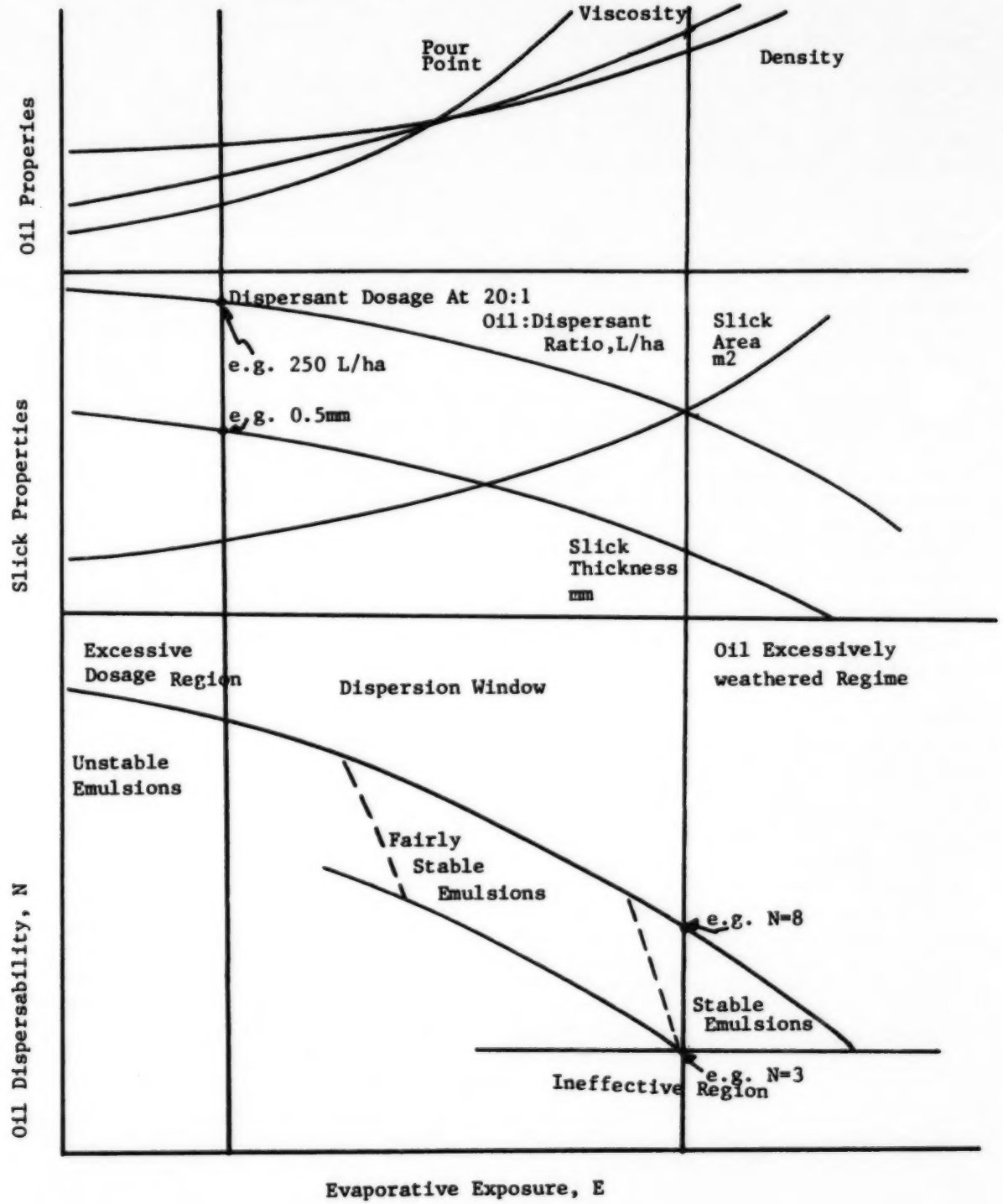


Figure 4.4 Consolidated plot of oil and slick properties and oil dispersability as a function of extent of weathering showing the dispersion time window



give viscous residues, this window may be quite short. Indeed in extreme cases it may not be open at all.

We suggest that what is needed is a series of determinations of diagrams such as Figure 4.4 for selected oils to build up a knowledge base as to how important and variable this effect may be. At present, information on the time window is fragmented and inadequately documented.

In the analysis of data from experimental spills, it would be useful to sample the surface slick from time to time, obtain GC analyses, and thus estimate the exposure which each part of the oil has experienced. If the dispersant dosage is also known, it should be possible to determine if the oil was inherently dispersable at the time of application. The capability could be built up of relating experimental spill dispersion to laboratory test dispersion.

The problem becomes much easier if the oil is contained in a boom prior to dispersion since the area and E are then known exactly.

A remaining and formidable difficulty is that of measuring the delivered dispersant to oil ratio. Although dyed dispersant dosage on cards can give an estimate of dispersant dosage (L/ha), probably the most reliable technique is to dope the oil and dispersant with known concentrations of water-insoluble chemicals or tracers and determine the ratio of these concentration in the dispersal oil. One possibility would be to use radio labelled hydrocarbons or organo-metallic compounds of the rare earth elements which could be detected by neutron activation analysis at very low concentrations.

Although it is unwise to speculate on the results of such tests, if it can be demonstrated that dispersant effectiveness remains lower than expected, even when delivered dispersant dosage is correct and the oil is not excessively weathered, then the only remaining factor is the nature of at-sea mixing/turbulence phenomena. It is conceivable that the turbulence present in the slick and potentially available to promote dispersion is not of the desired nature in terms of frequency, intensity, or length scale. Laboratory systems may fortuitously generate the desired type of turbulence. If this is the case (and it is hoped that it is not) then the entire issue of chemical dispersion as a countermeasure will require rethinking. Fortunately, the UK experience described by Turner and Hurford (1986) suggests that dispersants do result in mitigation of the adverse effects of oil spills, provided that the technical and decision infrastructure is in place well in advance of the emergency.

5. CONCLUSIONS

A series of exploratory tests have been conducted to elucidate the mixing phenomena which occur when dispersant drops land on, penetrate into, and mix with oil. The results show that the phenomena are quite complex, but it is believed that it should be possible to estimate or calculate F, a "fraction of dispersant which intimately mixes with the oil".

Dispersion tests have been conducted with the Double Tube Labofina or WSL and MNS apparatus and the results interpreted in terms of a performance factor N. ie. the volume of oil dispersed per unit volume of dispersant. It is believed that N is influenced by the nature of the dispersant and that of the oil, but that it falls as the oil weathers and increases in viscosity. It may also fall as a result of formation of a film or skin of viscous oil at the oil-water interface. Attempts have been made to identify and study this interface which have been only partially successful.

Dispersion data have been examined using a triangular diagram approach. This suggests that an important and hitherto under-appreciated effect is the capacity of the water to accommodate high concentrations of emulsion. It appears that oil in water concentrations of only about 0.4% can be achieved thus limiting dispersant effectiveness.

A method of quantifying N in terms of evaporative exposure has been devised which suggests that the time window for effective dispersion is quite short in some cases.

It is believed that if F, N, and the volume of "accessible" water can be quantified then reliable dispersion models or predictive capability could be devised, similar to that devised in earlier phases of this research program.

6. REFERENCES

Chau, A., Sproule, J., and Mackay, D., 1986, A Study of the Fundamental Mechanism of Chemical Dispersion of Oil Spill. Report to Environment Canada, Environmental Emergencies Branch, Ottawa.

Mackay, D. and Chau, A., 1986, The Effectiveness of Chemical Dispersants: A Discussion of Laboratory and Field Test Result. International Seminar on Chemical and Natural Dispersion of Oil on Sea, DOOS Proceedings 1986, Trondheim, Norway

Mackay, D., Chau, A., and Bobra, A., 1984, "What's New in Chemical Dispersants?", Proceedings of the Seventh Annual Arctic Marine Oil Spill Program Technical Seminar, pp257-277

Stiver, W., and Mackay, D., 1984, Evaporation Rate of Spills of Hydrocarbons and Petroleum Mixtures, Environ. Sci. Technol. 18, pp 834-840

Lindblom, G., 1986, Dispersants and Their Application as Currently Perceived in the United States., Paper presented at the International Seminar of Chemical Dispersion of Oil on Sea, DOOS Proceedings, Trondheim, Norway.

Turner, A., and Hurford, N., 1986, The use of Oil Spill Dispersants - Some Views from U.K., Paper presented at the International Seminar of Chemical Dispersion of Oil on Sea, DOOS Proceedings, Trondheim, Norway.

Nichols, J.A., and Parker, H.D., 1984, Dispersant Comparison of Laboratory Texts and Field Trials with Practical Experience at Spills, 1985 Oil Spill Conference Proceedings, pp. 421-427, Amer. Petrol. Inst., Washington, D.C.

Wallis, G.B., 1974, The Terminal Speed of Single Drop or Bubbles in an Infinite Medium, Int. J. of Multiphase Flow, Vol. 1, pp. 491-511, Pergamon Press.

Davies, J.T., and Mayers, G., 1960, Studies on the Interfacial Viscosities of Monolayers, Trans. Faraday Soc. 56, 691-696.

Lichtenthaler, R.G., and Daling, P.S., 1985, Chemical Application of Dispersants - Comparison of Slick Behaviour of Chemically Treated Versus Non-treated Slicks, 1985 Oil Spill Conference Proceedings, pp. 471-478, Amer. Petrol. Inst., Washington, D.C.

Martinelli, F.N., and Lynch, B.W.J., 1980, Factors Affecting the Efficiency of Dispersants, Warren Spring Laboratory, Report LR363.

Eicke, H.F., and Parfitt, G.D., 1987, Interfacial Phenomena in Apolar Media, Surfactant Science Series Vol. 21, Marcel Dekker Inc., N.Y.